

## DESCRIPTION

PERSONAL ORNAMENT HAVING WHITE COATING LAYER  
AND PROCESS FOR PRODUCING THE SAME

TECHNICAL FIELD

The present invention relates to a personal ornament having a white coating layer, and a process for producing the same. More particularly, the present invention relates to a low-priced personal ornament having an inexpensive white-colored stainless steel coating layer excellent in long-term corrosion resistance on the surface of a base article made of a less corrosive metal or alloy thereof; and a process for producing the personal ornament.

## BACKGROUND OF THE INVENTION

Heretofore, many personal ornaments such as watches, necklaces, pendants, and brooches are made from a copper alloy owing to workability, material cost, and other reasons.

However, a personal ornament made from a copper alloy, which is less corrosion-resistant, as the base material is usually covered with a plating layer formed by wet plating to protect the base material from corrosion.

25 This plating layer is usually constituted of an underlying

nickel plating layer formed by wet plating and an outermost plating layer formed thereon by wet plating. For making the outermost layer golden in color, a gold plating layer is formed on the nickel layer by wet plating.

- 5 For making the outermost layer white in color tone, a palladium plating layer, a palladium alloy plating layer, or a rhodium plating layer is formed on the nickel layer by wet plating. The plating layer is generally formed in a thickness ranging from 1 to 5  $\mu$ m.

- 10 The aforementioned personal ornaments, however, have disadvantage of high cost owing to the noble metal-containing outermost plating layer for corrosion resistance. Therefore, low-priced personal ornaments naturally have a thin outermost plating layer, lacking in
- 15 long-term corrosion resistance. Moreover, in the production of the low-priced ornaments, the noble metal plating bath should be strictly controlled and maintained in order to obtain stably a thin outermost plating layer, and the workers for the plating operation should have high
- 20 skill in order to obtain stably the outermost plating layer of the desired color tone. Furthermore, a personal ornament having a characteristic white color of the stainless steel has not yet been produced at a low price.

- Accordingly, there are demanded a low-priced
- 25 personal ornament having an inexpensive white-colored

stainless steel coating layer excellent in long-term corrosion resistance on the surface of a base article made of a less corrosive metal or alloy thereof; and a process for producing the personal ornament.

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~~OBJECT OF THE INVENTION~~

The present invention has been made to solve the problems of the aforementioned prior art techniques, and an object of the present invention is to provide a low-priced personal ornament having an inexpensive white-colored stainless steel coating layer excellent in long-term corrosion resistance on the surface of a base article made of a less corrosive metal or alloy thereof; and a process for producing the personal ornament.

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SUMMARY OF THE INVENTION  
~~DISCLOSURE OF THE INVENTION~~

The first personal ornament having a white coating layer of the present invention comprises

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a base article of the personal ornament made of a metal, and

a white-colored stainless steel coating layer formed by a dry plating process on at least a part of the surface of the base article.

The above base article of the personal ornament is made usually of tungsten carbide or tantalum carbide.

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The second personal ornament having a white coating layer of the present invention comprises:

a base article of the personal ornament made of a nonferrous metal,

5 an underlying plating layer formed on the surface of the base article, and

a white-colored stainless steel coating layer formed by a dry plating process on at least a part of the surface of the underlying plating layer.

10 The base article of the personal ornament of the second embodiment is made usually of at least one nonferrous metal selected from the group consisting of copper, copper alloys, aluminum, aluminum alloys, zinc, zinc alloys, magnesium, and magnesium alloys.

15 The first or second personal ornament having a white coating layer of the present invention may have, on the surface of the stainless steel coating layer, a white-colored noble metal coating layer in a thickness ranging from 0.04 to 0.3  $\mu\text{m}$  formed by a dry plating process.

20 The underlying plating layer may have a multilayer structure constituted of at least one plating layer formed by a wet plating process, and at least one different plating layer formed by a dry plating process.

The underlying plating layer is preferably a  
25 coating layer formed by a wet plating process and composed

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of at least one metal selected from the group consisting of gold, copper, nickel, chromium, tin, palladium, nickel-phosphorus alloys, nickel alloys excluding nickel-phosphorus alloys, copper-tin-palladium alloys, copper alloys excluding copper-tin-palladium alloys, tin alloys excluding copper-tin-palladium alloys, and palladium alloys excluding copper-tin-palladium alloys.

The nickel-phosphorus alloy plating layer as the underlying plating layer is preferably a hard coating layer having been treated for age hardening.

For prevention of development of nickel allergy, the underlying plating layer preferably contains no nickel. Such an underlying plating layer is composed preferably of at least one nickel-free metal selected from the group consisting of gold, copper, chromium, tin, palladium, copper-tin-palladium alloys, copper alloys excluding copper-tin-palladium alloys, tin alloys excluding copper-tin-palladium alloys, and palladium alloys excluding copper-tin-palladium alloys, and is formed by a wet plating process.

The underlying plating layer is preferably a coating layer formed by a dry plating process and is composed of titanium carbide, zirconium carbide, or tantalum carbide.

The entire thickness of the underlying plating

layer is usually in the range of from 0.2 to 30  $\mu$ m.

In the first and second personal ornament having a white coating layer of the present invention, the white-colored stainless steel coating layer is composed

5 preferably of an austenitic stainless steel, particularly an austenitic stainless steel having a composition of 0.01-0.12 vol% of carbon, 0.1-1.0 vol% of silicon, 1.0-2.5 vol% of manganese, 8-22 vol% of nickel, and 15-26 vol% of chromium.

10 For prevention of development of nickel allergy, the white-colored stainless steel layer preferably contains no nickel. Such a white-colored stainless steel coating layer is composed preferably of a nickel-free ferritic stainless steel, particularly nickel-free  
15 ferritic stainless steels having a composition of 0.01-0.12 vol% of carbon, 0.1 -1.0 vol% of silicon, 1.0-2.5 vol% of manganese, 14-20 vol% of chromium, and 0.4-2.5 vol% of molybdenum.

The above white-colored stainless steel coating  
20 layer can be formed by a dry plating process selected from a sputtering method, an arc evaporation method or an ion-plating method.

In the first or second personal ornament having a white coating layer of the present invention, on the  
25 surface of the base article or of the underlying plating

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layer, at least one plating layer different in color tone from the white-colored stainless steel coating layer may be formed by a dry plating process in addition to the stainless steel coating layer formed by a dry plating process.

The plating layer different from the stainless steel coating layer is preferably a coating layer composed of gold, a gold alloy, titanium nitride, or zirconium nitride.

The first process for producing a personal ornament having a white coating layer of the present invention comprises the steps of:

forming a base article of the personal ornament from a metal (or an alloy) by machining,

washing and degreasing the surface of the base article,

setting the base article in a dry plating apparatus selected from sputtering systems (apparatuses), arc evaporation systems (apparatuses), and ion-plating systems (apparatuses), and cleaning the base article by bombard cleaning in an argon gas atmosphere, and

forming a white-colored stainless steel coating layer on the base article by a dry plating process.

The metal employed for forming the base article of the above personal ornament is usually tungsten carbide or

tantalum carbide.

The second process for producing a personal ornament having a white coating layer of the present invention comprises the steps of:

5        forming a base article of the personal ornament from a nonferrous metal (or an alloy) by machining; washing and degreasing the surface of the base article;

10       forming on the surface of the base article an underlying plating layer by a wet plating process or a dry plating process;

15       setting the base article having the underlying plating layer in a dry plating apparatus selected from sputtering systems, arc evaporation systems, and ion-plating systems, and cleaning the surface of the underlying plating layer by bombard cleaning in an argon gas atmosphere; and

20       forming a white-colored stainless steel coating layer by a dry plating process on the surface of the underlying plating layer.

25       The nonferrous metal employed for forming the base article of the above personal ornament is at least one nonferrous metal selected from the group consisting of copper, copper alloys, aluminum, aluminum alloys, zinc, zinc alloys, magnesium, and magnesium alloys.

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In the first or second process for producing a personal ornament having a white coating layer of the present invention, the process may further comprise, after the step of forming the white-colored stainless steel coating layer, a step of forming a white-colored noble metal coating layer in a thickness ranging from 0.04 to 0.3  $\mu\text{m}$  on the surface of the stainless steel coating layer by a dry plating process.

The underlying plating layer may have a multilayer structure constituted of at least one plating layer formed by a wet plating process on the surface of the base article, and at least one plating layer formed thereon by a dry plating process.

The underlying plating layer is preferably formed by a wet plating process from at least one metal selected from the group consisting of gold, copper, nickel, chromium, tin, palladium, nickel-phosphorus alloys, nickel alloys excluding nickel-phosphorus alloys, copper-tin-palladium alloys, copper alloys excluding copper-tin-palladium alloys, tin alloys excluding copper-tin-palladium alloys, and palladium alloys excluding copper-tin-palladium alloys.

In the case where a nickel-phosphorus alloy is employed as the underlying plating layer, the nickel-phosphorus alloy plating layer is preferably treated for

age hardening at 200 to 450°C for 20 to 60 minutes to harden the nickel-phosphorus alloy plating layer.

For prevention of development of nickel allergy, the underlying plating layer is preferably formed by a wet plating process from at least one nickel-free metal selected from the group consisting of gold, copper, chromium, tin, palladium, copper-tin-palladium alloys, copper alloys excluding copper-tin-palladium alloys, tin alloys excluding copper-tin-palladium alloys, and palladium alloys excluding copper-tin-palladium alloys.

The underlying plating layer is preferably formed from titanium carbide, zirconium carbide, or tantalum carbide by a dry plating process.

The entire thickness of the underlying plating layer is usually in the range of 0.2 to 30  $\mu\text{m}$ .

In the first and second process of forming a personal ornament having a white coating layer of the present invention, the white-colored stainless steel coating layer is preferably an austenitic stainless steel, particularly an austenitic stainless steel having a composition of 0.01-0.12 vol% of carbon, 0.1-1.0 vol% of silicon, 1.0-2.5 vol% of manganese, 8-22 vol% of nickel, and 15-26 vol% of chromium, and is formed by a sputtering method, an arc evaporation method, or an ion plating method.

For prevention of nickel allergy, the white-colored stainless steel preferably contains no nickel. Such a white-colored stainless steel coating layer is composed preferably of a ferritic stainless steel not containing nickel, particular a ferritic stainless steel not containing nickel having a composition of 0.01-0.12 vol% of carbon, 0.10-1.0 vol% of silicon, 1.0-2.5 vol% of manganese, 14-20 vol% of chromium and 0.4-2.5 vol% of molybdenum, and is formed by a sputtering method, an arc evaporation method or an ion plating method.

The first or second process for producing a personal ornament having a white coating layer of the present invention further comprises, after the steps of forming a white-colored stainless steel coating layer on the surface of the ornament base article or of the underlying coating layer, at least once the steps of masking a part of the stainless steel coating layer, forming a plating layer different in color tone from the stainless steel coating layer on the surface of the stainless steel coating layer and the surface of the mask by a dry plating process, and removing the mask and the coating layer on the mask, to thereby provide an outermost plating layer (finish-plating layer) having a white-colored stainless steel coating layer portion and at least one plating layer portion different in color tone from the

stainless steel coating layer.

The plating layer different in color tone from the stainless steel coating layer is preferably obtained by forming at least one coating layer from a metal selected from the group consisting of gold, gold alloys, titanium nitride, hafnium nitride, and zirconium nitride by a dry plating process selected from sputtering methods, arc evaporation methods, and ion plating methods.

#### BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a schematic illustration of an abrasion resistance tester for explaining the method of the abrasion resistance test.

### DETAILED DESCRIPTION OF THE INVENTION

#### BEST MODE FOR CARRYING OUT THE INVENTION

The personal ornament having a white coating layer and the process for producing the personal ornament of the present invention are described below in more detail.

The first personal ornament having a white coating layer of the present invention is constituted of a base article of the personal ornament and a white-colored stainless steel coating layer as the outermost coating layer (finish-plating layer).

The second personal ornament having a white coating layer of the present invention is constituted of a base



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The present invention includes a personal ornament having an outermost coating layer entirely formed of stainless steel coating layer, or an another personal ornament having an outermost coating layer formed of stainless steel layer to one portion and of one or more coating layer(s) different in color tone from the stainless steel coating layer to another portion.

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alloys, zinc, zinc alloys, magnesium, and magnesium alloys.

The base article of a personal ornament  
(hereinafter referred to "ornament base article") is  
shaped from the above metal or nonferrous metal by a  
5 conventional machining process.

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The personal ornaments (and parts thereof) includes  
watchcases, watchbands, watch crowns, watch buckles, belt  
buckles, finger rings, necklaces, bracelets, earrings,  
pendants, brooches, cuff buttons, necktie holders, badges,  
10 medals, and eyeglass bows.

The first personal ornament having a white coating  
layer of the present invention has a white-colored  
stainless steel coating layer formed by a dry plating  
process directly on the surface of the ornament base  
15 article. The second personal ornament having a white  
coating layer of the present invention has a white-colored  
stainless steel coating layer formed by a dry plating  
process on the surface of the underlying plating layer  
formed on the surface of the ornament base article.

20 In the present invention, before forming the  
stainless steel coating layer or the underlying plating  
layer on the ornament base article surface, the surface of  
the ornament base article is preferably washed and  
degreased by the use of a conventional organic solvent or  
25 the like.

Underlying Plating Layer

The underlying plating layer of the second personal ornament having a white coating layer of the present invention is a plating layer formed by a wet plating  
5 process or a dry plating process. The underlying plating layer may be of a multilayer structure constituted of one or more plating layers formed by a wet plating process and one or more plating layers formed by a dry plating process.

Examples of the underlying plating layer include:

10 an underlying plating layer of a two-layer structure constituted of a gold plating layer (flash plating) formed by a wet plating process and a titanium plating layer formed by a dry plating process;

an underlying plating layer of a three-layer  
15 structure constituted of a copper plating layer formed by a wet plating process, a copper-tin plating layer formed by a wet plating process, and a titanium carbide plating layer formed by a dry plating process;

an underlying plating layer of a three-layer  
20 structure constituted of a palladium plating layer (flash plating), a titanium plating layer formed by a dry plating process, and a titanium carbide plating layer formed by a dry plating process;

an underlying plating layer of a four-layer  
25 structure constituted of a copper-tin alloy plating layer

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formed by a wet plating process, a copper-tin-zinc alloy plating layer formed by a wet plating process, a gold strike plating layer formed by a wet plating process, and a titanium plating layer formed by a dry plating process;

5 and

an underlying plating layer of a five-layer structure constituted of a copper-tin alloy plating layer formed by a wet plating process, a copper-tin-zinc alloy plating layer formed by a wet plating process, a palladium strike plating layer formed by a wet plating process, a titanium plating layer formed by a dry plating process, and a titanium carbide plating layer formed by a dry plating process.

The underlying plating layer may also be constituted of two or more plating layers formed by a wet plating process on the surface of an ornament base article.

Examples of this type of underlying plating layer include:

an underlying plating layer of a two-layer structure constituted of a nickel strike plating layer (flash plating) and a nickel plating layer;

an underlying plating layer of a two-layer structure constituted of a nickel plating layer, and a nickel-phosphorus alloy plating layer;

25 an underlying plating layer of a two-layer

structure constituted of a copper plating layer and a copper-tin-palladium alloy plating layer;

an underlying plating layer of a two-layer structure constituted of a copper-tin alloy plating layer and a copper-tin-palladium alloy plating layer;

an underlying plating layer of a two-layer structure constituted of a copper-tin alloy plating layer and a copper-tin-zinc alloy plating layer;

an underlying plating layer of a three-layer structure constituted of a copper-tin alloy plating layer, a copper-tin-palladium alloy plating layer, and a gold plating layer (flash plating);

an underlying plating layer of a three-layer structure constituted of a copper-tin alloy plating layer, a copper-tin-zinc alloy plating layer, and a gold strike plating layer;

an underlying plating layer of a three-layer structure constituted of a copper-tin alloy plating layer, a copper-tin-zinc alloy plating layer, and a palladium strike plating layer;

an underlying plating layer of a three-layer structure constituted of a nickel plating layer, a nickel-phosphorus alloy plating layer, and a palladium-nickel alloy plating layer;

an underlying plating layer of a four-layer

structure constituted of a nickel strike plating layer (flash plating), a nickel plating layer, a nickel-phosphorus alloy plating layer, and a palladium-nickel alloy plating layer (flash plating);

5 an underlying plating layer of a four-layer structure constituted of a nickel strike plating layer (flash plating), a nickel plating layer, a nickel-phosphorus alloy plating layer, and a palladium strike plating layer;

10 an underlying plating layer of a four-layer structure constituted of a copper plating layer, a copper-tin alloy plating layer, a copper-tin-palladium alloy plating layer, and a palladium plating layer (flash plating); and

15 an underlying plating layer of a four-layer structure constituted of a copper plating layer, a copper-tin alloy plating layer, a copper-tin-zinc alloy plating layer, and a palladium strike plating layer.

20 The entire thickness of the underlying plating layer ranges usually from 0.2 to 30  $\mu\text{m}$ , preferably from 0.5 to 30  $\mu\text{m}$ , more preferably from 5 to 20  $\mu\text{m}$ . For example, in the underlying plating layer of two or more layer structure comprising a copper-tin alloy plating layer and a copper-tin-zinc alloy plating layer, the copper-tin  
25 alloy plating layer has a thickness usually ranging from 1

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to 5  $\mu$ m, and the copper-tin-zinc alloy plating layer has a thickness ranging from 1 to 5  $\mu$ m.

The aforementioned underlying plating layer formed by a wet plating process is specifically composed of at least one metal selected from the group consisting of gold, copper, nickel, chromium, tin, palladium, nickel-phosphorus alloys, nickel alloys excluding nickel-phosphorus alloys, copper-tin-palladium alloys, copper alloys excluding copper-tin-palladium alloys, tin alloys excluding copper-tin-palladium alloys, and palladium alloys excluding copper-tin-palladium alloys. The nickel-phosphorus alloy layer is preferably a hard coating layer having been treated for age hardening.

For prevention of development of nickel allergy, the underlying plating layer is preferably formed by a wet plating process and contains no nickel. Specifically, the underlying plating layer is composed preferably of at least one nickel-free metal selected from the group consisting of gold, copper, chromium, tin, palladium, copper-tin-palladium alloys, copper alloys excluding copper-tin-palladium alloys, tin alloys excluding copper-tin-palladium alloys, and palladium alloys excluding copper-tin-palladium alloys.

The nickel alloys excluding nickel-phosphorus alloys include specifically nickel-cobalt alloys, nickel-

copper alloys, nickel-iron alloys, nickel-palladium alloys, gold-nickel alloys, and tin-nickel alloys.

The copper alloys excluding copper-tin-palladium alloys include specifically copper-tin-zinc alloys, copper-tin alloys, copper-gold alloys, copper-silver alloys, and copper-gold-silver alloys.

The tin alloys excluding copper-tin-palladium alloys include specifically copper-tin-zinc alloys, copper-tin alloys, palladium-tin alloys, tin-nickel alloys, and tin-gold alloys.

The palladium alloys excluding copper-tin-palladium alloys include specifically palladium-nickel alloys, palladium-cobalt alloys, palladium-silver alloys, palladium-tin alloys, palladium-iron alloys, and palladium-gold alloys.

The underlying plating layer, for example a nickel plating layer, is formed on the surface of the ornament base article by a wet plating process specifically by the use of a plating solution containing nickel metallic ion.

The embodiments of the nickel plating layer in the present invention are described below as examples.

(First Embodiment)

A first embodiment of the nickel plating layer in the present invention is a bright nickel plating layer formed on the aforementioned base article by



electroplating in a bright nickel plating solution (Watt bath). The solution contains 150-400 g/lit., preferably 250-300 g/lit. of nickel sulfate ( $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ), 20-60 g/lit., preferably 40-50 g/lit. of nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ), 10-50 g/lit., preferably 30-40 g/lit. of boric acid ( $\text{H}_3\text{BO}_3$ ) and a brightening agent (a commercial product, e.g., Brightener #61 (standard addition amount: 0.5 ml/lit.), #62 (standard addition amount: 4 ml/lit.), and #63 (standard addition amount: 10 ml/lit.), produced by Ebara-Udylite Co., Ltd.).

This plating solution is an acidic solution having a pH of 4.0-4.5, preferably 4.0-4.3. The aforementioned nickel plating layer can be formed by electroplating in the aforementioned plating solution under the conditions of a bath temperature of 40-50°C, and a current density (Dk) of 1-3 A/dm<sup>2</sup>.

(Second Embodiment)

A second embodiment of the nickel plating layer in the present invention is a semi-bright nickel plating layer formed on the aforementioned base article by electroplating in a semi-bright nickel plating solution. The solution contains 150-400 g/lit., preferably 250-300 g/lit. of nickel sulfate ( $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ), 20-60 g/lit., preferably 40-50 g/lit. of nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ), 10-50 g/lit., preferably 30-40 g/lit. of boric acid ( $\text{H}_3\text{BO}_3$ )

and a semi-brightening agent (a commercial product, e.g., semi-brightener Levenon A (standard addition amount: 5 ml/lit.), produced by Nikko Metal Co.).

5 This plating solution is an acidic solution having a pH of 4.0-4.5, preferably 4.0-4.3. The aforementioned nickel plating layer can be formed by electroplating in the aforementioned plating solution under the conditions of a bath temperature of 40-50°C, and a current density (Dk) of 1-3 A/dm<sup>2</sup>.

10 <Third Embodiment>

A third embodiment of the nickel plating layer in the present invention is a nickel plating layer formed on the aforementioned base article by electroplating in a nickel strike plating solution. The solution contains  
15 150-300 g/lit., preferably 200-250 g/lit. of nickel chloride (NiCl<sub>2</sub>·6H<sub>2</sub>O) and 100-150 g/lit., preferably 125±10 g/lit. of hydrochloric acid (HCl).

This plating solution is an acidic solution having a pH of lower than 1.0. The aforementioned nickel plating  
20 layer can be formed by electroplating in the aforementioned plating solution under the conditions of a bath temperature of 25±2°C, and a current density (Dk) of 3-5 A/dm<sup>2</sup>.

In the case where the underlying plating layer is a  
25 nickel-phosphorus alloy plating layer, this plating layer

is formed by a wet plating process on the surface of the ornament base article. This plating layer is composed of an amorphous nickel-phosphorus alloy as it is formed, and can be crystallized by age hardening treatment mentioned

5 later to be a hard coating layer. This age hardening treatment may be conducted concurrently with, or after the formation of the outermost coating layer (finish-plating layer). Otherwise, the nickel-phosphorus alloy plating layer may be treated for age hardening after the formation  
10 thereof in an ion plating apparatus or a sputtering apparatus before the formation of the outermost coating layer by ion plating or sputtering in the same apparatus.

The phosphorus content in the nickel-phosphorus alloy plating layer ranges preferably from 13 to 15 wt%.

15 The nickel-phosphorus alloy plating layer is formed, for example, by electroplating the surface of the ornament base article in a plating solution containing 100-200 g/lit., preferably 140-160 g/lit. of nickel sulfate ( $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ ), 10-40 g/lit., preferably 20-30 g/lit. of  
20 nickel hydroxide ( $(\text{Ni}(\text{OH})_2 \cdot \text{H}_2\text{O})$ ), 1-10 g/lit., preferably 4-6 g/lit. of sodium hypophosphite ( $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ ), 50-90 ml/lit., preferably 65-75 ml/lit. of phosphoric acid ( $\text{H}_3\text{PO}_4$ ) and 50-150 g/lit., preferably 90-110 g/lit. of sodium citrate.

25 This plating solution is an acidic solution having

5 a pH of 2.8-3.2. The nickel-phosphorus alloy plating layer can be formed by electroplating in the aforementioned plating solution under the conditions of a bath temperature of 60-80°C, and a current density (Dk) of 1.0-3.0 A/dm<sup>2</sup>, preferably 2.0±0.2 A/dm<sup>2</sup>.

10 In the present invention, the nickel-phosphorus alloy plating layer containing a phosphorus content of 13-15 wt% can be formed by selecting the conditions of the hypophosphorus acid concentration in the plating solution, the sodium citrate concentration in the plating solution, the pH of the plating solution, and the current density to be in the range as mentioned above.

15 The sodium hypophosphite and the phosphoric acid serve as a reducing agent and supply phosphorus for constituting the nickel-phosphorus alloy plating layer.

The nickel hydroxide serves as a pH adjusting agent and the sodium citrate serves as a complexing agent.

20 On the other hand, the underlying plating layer formed by the aforementioned dry plating process includes preferably white-colored plating layers formed from titanium carbide, zirconium carbide, or tantalum carbide. Before forming such a plating layer, a titanium plating layer may be formed on the surface of the base article or the wet-plated layer. The formation of this titanium  
25 plating layer improves the adhesiveness between the base

article adjacent to the titanium plating layer and the dry-plated later, or the adhesiveness between the wet-plated layer adjacent to the titanium plating layer and the dry-plated layer.

5       The dry plating process includes specifically physical vapor deposition (PVD) such as sputtering methods, arc evaporation methods, ion-plating methods, and ion beam processes; and CVD. Of these, sputtering methods, arc evaporation methods, and ion-plating methods are  
10 particularly preferred.

#### Outermost Coating Layer

(Stainless Steel Coating Layer)

The outermost coating layer constituting the first or second personal ornament having a white coating layer  
15 of the present invention has a white-colored stainless steel coating layer formed by a dry plating process on at least a part of the surface of the ornament base article or of the underlying plating layer.

In the present invention, before the formation of  
20 the stainless steel coating layer, the surface of the ornament base article or the underlying coating layer is preferably cleaned by a bombard cleaning method in an argon gas atmosphere in a dry plating apparatus selected from sputtering systems, arc evaporation systems, and ion-  
25 plating systems.

The white-colored stainless steel coating layer is a plating layer composed preferably of an austenitic stainless steel, particularly an austenitic stainless steel having a composition of 0.01-0.12 vol% of carbon, 0.1-1.0 vol% of silicon, 1.0-2.5 vol% of manganese, 8-22 vol% of nickel, and 15-26 vol% of chromium (e.g., SUS310S, and SUS304 (JIS Standard)).

For prevention of development of nickel allergy, the white colored stainless steel preferably contains no nickel. Such a white-colored stainless steel coating layer is composed preferably of a nickel-free ferritic stainless steel, particularly a nickel-free ferritic stainless steel having a composition of 0.01-0.12 vol% of carbon, 0.1 -1.0 vol% of silicon, 1.0-2.5 vol% of manganese, 14-20 vol% of chromium, and 0.4-2.5 vol% of molybdenum (e.g., SUS444 (JIS Standard)).

Before forming such a stainless steel coating layer, a titanium plating layer may be formed by a dry plating process on the surface of the base article or the underlying plated layer. The formation of this titanium plating layer improves the adhesiveness between the base article adjacent to the titanium plating layer and the stainless steel coating layer, or the adhesiveness between the underlying layer adjacent to the titanium plating layer and the stainless steel coating layer.

The dry plating process for forming the stainless steel coating layer includes sputtering methods, arc evaporation methods, and ion-plating methods.

The thickness of the white-colored stainless steel coating layer is in the range of usually  $0.1-2.0\mu\text{m}$ , preferably  $0.2-1.2\mu\text{m}$ , more preferably  $0.3-0.7\mu\text{m}$ .

(Plating Layer Different in Color Tone from Stainless Steel Coating Layer)

In the first or second personal ornament having a white coating layer of the present invention, at least one plating layer different in color tone from the white colored stainless steel coating layer may be formed by a dry plating process in addition to the white-colored stainless steel coating layer on the surface of the ornament base article or the underlying plating layer.

The personal ornament having, a plating layer, as the outermost coating layer, different in color tone from the white-colored stainless steel coating layer can be produced, for example, through the process below.

First, a white-colored stainless steel coating layer is formed on the surface of the ornament base article or of the underlying coating layer. Then, the steps of masking a part of the surface of the stainless steel coating layer, forming a plating layer different in color tone from the stainless steel coating layer on the

surface of the stainless steel coating layer and the surface of the mask by a dry plating process, and removing the mask together with the plating layer thereon are carried out at least one time. Thus, there can be

5 obtained an outermost coating layer of two or more color tones comprising a white-colored stainless steel coating layer portion and at least one plating layer portion different in color tone from the stainless steel coating layer.

10 The plating layer different in color tone from the stainless steel coating layer is preferably obtained by forming at least one coating layer comprising a metal selected from the group consisting of gold, gold alloys, titanium nitride, and zirconium nitride by a dry plating  
15 process selected from a sputtering method, an arc evaporation method, and an ion plating method.

The thickness of the plating layer different in color tone from the stainless steel coating layer is in the range of usually  $0.1-1.0\mu\text{m}$ , preferably  $0.2-0.5\mu\text{m}$ .

20 (Noble Metal Coating Layer)

The personal ornament having a white coating layer of the present invention may have additionally a white-colored noble metal coating layer in the thickness range of  $0.04-0.3\mu\text{m}$ , preferably  $0.05-0.2\mu\text{m}$  formed by a dry  
25 plating process on the aforementioned stainless steel



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hardening treatment to the nickel-phosphorus alloy plating layer may be conducted after the formation thereof and before the formation of the outermost coating layer, by ion plating, sputtering or arcing in the same apparatus for the ion plating, sputtering, or arcing for the formation of the outermost coating.

The age hardening treatment is conducted at a treatment temperature of usually 200-450°C, preferably 250-430°C, more preferably 300-400°C, for a treatment time of usually 20-60 minutes, preferably 25-55 minutes, more preferably 30-50 minutes.

The age hardening treatment of the nickel-phosphorus alloy plating layer can be conducted concurrently with the formation of the outermost coating layer by selecting the conditions of the ion plating, sputtering or arc evaporation method for the formation of the outermost coating layer so as to coincide with the heat treatment conditions for the above age hardening treatment.

In the case where the conditions of the dry plating process such as an ion plating method for the formation of the outermost coating layer are selected to be lower than the lower limit of the thermal treatment conditions of the above age hardening, the age hardening treatment is to be conducted under the aforementioned thermal treatment

conditions after the formation of the surface coating layer.

In the present invention, the age hardening treatment of the nickel-phosphorus alloy plating layer is preferably conducted simultaneously with the formation of the outermost coating layer in view of the productivity. The age hardening treatment is preferably conducted in a vacuum.

When an amorphous nickel-phosphorus alloy plating layer is subjected to age hardening treatment, the amorphous matter in the nickel-phosphorus alloy plating layer is crystallized to turn the nickel-phosphorus alloy plating layer into a hard coating layer.

#### EFFECTS OF THE INVENTION

The present invention provides a white-colored stainless steel coating layer as an outermost coating layer which is inexpensive and is corrosion-resistant for a long term; a low-priced personal ornament having a white-colored noble metal coating layer on the surface of the stainless steel coating layer; and a process for producing the same.

In the present invention, as the outermost coating layer, a plating layer composed of an expensive noble metal such as gold may be formed as a plating layer different in color tone from the stainless steel coating

layer in addition to the inexpensive stainless steel coating layer. The formation of the noble metal plating layer on a limited area of the surface of the personal ornament can lower the price of the personal ornament.

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#### EXAMPLES

The present invention is described by reference to examples without limiting the invention in any way.

10 The corrosion resistance test in the examples was conducted in a manner shown below.

#### (Corrosion Resistance Test of Plating Layer)

15 The corrosion resistance test of the plating layer was conducted according to JIS H 8502 (CASS test). The test was continued for 96 hours. The surface of the plating layer after the corrosion test was evaluated to be "good" when the rating number was not lower than 9.8 according to the rating number standard diagram.

#### (Example 1)

20 A base article of a watchcase was shaped from tungsten carbide by machining. This base article was washed and degreased with an organic solvent.

This base article was set in a sputtering apparatus, and the surface of the base article was cleaned by bombard  
25 cleaning in an argon atmosphere.

On the surface of this base article, a white-colored stainless steel coating layer was formed in a thickness of  $0.2\mu\text{m}$  by a sputtering method (magnetron sputtering method) under the layer formation conditions below to obtain a watchcase.

Separately, in the same manner as above, on the surface of another base article, a white-colored stainless steel coating layer was formed in a thickness of  $2\mu\text{m}$  to obtain another watchcase.

10 (Layer Formation Conditions)

Target:	Austenitic stainless steel SUS304
Sputtering gas:	Argon gas
Layer formation pressure:	0.2-0.9 Pa
Target power:	1.0-2.0 kW
15 Bias voltage:	Ground to -300 V

The resulting watchcases were tested for the corrosion resistance of the plating layer according to the aforementioned method. The rating numbers were not lower than 9.8, showing that the corrosion resistance was "good".

20 (Example 2)

A base article of a watchcase was shaped from brass by machining. This base article was washed and degreased with an organic solvent.

25 This base article was immersed in a plating

solution having the composition below. A nickel strike plating layer (flash plating) was formed in a thickness of 0.1-0.2  $\mu\text{m}$  on the base article surface by electroplating under the plating conditions below. The plated article

5 was washed with water.

«Nickel Strike Plating»

〈Plating Solution Composition〉

Nickel chloride 180 g/lit.

Hydrochloric acid 100 g/lit.

10 〈Plating Conditions〉

pH <1 (specifically 0.3 to less than 1)

Solution temperature Room temperature

Current density (Dk) 3-5 A/dm<sup>2</sup>

Time 30-60 seconds

15 This watchcase base article having the nickel strike plating layer was immersed in a plating solution having the composition below. A nickel plating layer was formed in a thickness of 2  $\mu\text{m}$  on the nickel strike plating layer surface by electroplating under the plating

20 conditions below. The plated base article was washed with water.

«Nickel Plating»

〈Plating Solution Composition〉

Nickel sulfate 250 g/lit.

25 Nickel chloride 75 g/lit.

Boric acid 50 g/lit.

Brightener (Brightener #61, produced by Ebara-Udylite Co., Ltd.)

0.5 ml/lit.

5 (Plating Conditions)

pH 3.6-4.0

Solution temperature 40-50°C

Current density (Dk) 3 A/dm<sup>2</sup>

10 This plated base article was set in a sputtering apparatus, and the surface of the base article was cleaned by bombard cleaning in an argon atmosphere.

On the surface of the nickel plating layer formed on this base article, a white-colored stainless steel coating layer was formed in a thickness of 0.5  $\mu$ m by a sputtering method under the layer formation conditions below to obtain a watchcase.

(Layer Formation Conditions)

Target: Austenitic stainless steel SUS304

Sputtering gas: Argon gas

20 Layer formation pressure: 0.2-0.9 Pa

Target power: 1.0-2.0 kW

Bias voltage: Ground to -300 V

The resulting watchcase was tested for the corrosion resistance of the plating layer according to the  
25 aforementioned method. The rating numbers were not lower

than 9.8, showing that the corrosion resistance was "good".

(Example 3)

A base article of a watchband was shaped from brass by machining. This base article was washed and degreased with an organic solvent.

This base article was immersed in a plating solution having the composition below. A nickel strike plating layer (flash plating) was formed in a thickness of 0.1-0.2  $\mu\text{m}$  on the base article surface by electroplating under the plating conditions below. The plated article was washed with water.

«Nickel Strike Plating»

〈Plating Solution Composition〉

15	Nickel chloride	180 g/lit.
	Hydrochloric acid	100 g/lit.

〈Plating Conditions〉

	pH	<1 (specifically 0.3 to less than 1)
	Solution temperature	Room temperature
20	Current density (Dk)	3-5 A/dm <sup>2</sup>
	Time	30-60 seconds

This watchband base article having the nickel strike plating was immersed in a plating solution having the composition below. A nickel plating layer was formed in a thickness of 2  $\mu\text{m}$  on the nickel strike plating layer



surface by electroplating under the plating conditions below. The plated article was washed with water.

### 《Nickel Plating》

#### 〈Plating Solution Composition〉

5	Nickel sulfate	250 g/lit.
	Nickel chloride	75 g/lit.
	Boric acid	50 g/lit.
	Brightener (Brightener #61, produced by Ebara-Udylite Co., Ltd.)	
10		0.5 ml/lit.

#### 〈Plating Conditions〉

pH	3.6-4.0
Solution temperature	40-50°C
Current density (Dk)	3 A/dm <sup>2</sup>

15 This watchband base article having the nickel plating layer was immersed in a plating solution having the composition below. A nickel-phosphorus alloy plating layer was formed in a thickness of 2  $\mu$ m on the nickel plating layer surface by electroplating under the plating conditions below. The plated base article was washed with water.

### 《Nickel-Phosphorus Alloy Plating》

#### 〈Plating Solution Composition〉

	Nickel sulfate	40-50 g/lit.
25	Nickel hydroxide	10-20 g/lit.

Sodium hypophosphite	3-10 g/lit.
Phosphoric acid	10-20 ml/lit.
Sodium citrate	30-50 g/lit.

〈Plating Conditions〉

5	pH	2.6-3.2
	Solution temperature	55°C
	Current density (Dk)	2 A/dm <sup>2</sup>

This watchband base article having the nickel-phosphorus alloy plating layer was immersed in a plating solution having the composition below. A palladium-nickel alloy plating layer (flash plating) was formed in a thickness of 0.1-0.2 μm on the nickel-phosphorus plating layer surface by electroplating under the plating conditions below. The plated base article was washed with water, and dried.

《Palladium-Nickel Alloy Plating》

〈Plating Solution Composition〉

Palladium	7.5 g/lit.
Nickel	12.5 g/lit.

20 〈Plating Conditions〉

pH	8
Solution temperature	32°C
Current density (Dk)	1.0 A/dm <sup>2</sup>
Specific gravity (Be)	12.5
25 Layer forming rate	4.2 minutes/1 μm

This plated base article was set in a sputtering apparatus, and the surface of the base article was cleaned by bombard cleaning in an argon atmosphere.

On the surface of the palladium-nickel alloy plating layer formed on this base article, a white-colored stainless steel coating layer was formed in a thickness of  $0.5\mu\text{m}$  by a sputtering method under the layer formation conditions below.

〈Layer Formation Conditions〉

10	Target:	Austenitic stainless steel SUS304
	Sputtering gas:	Argon gas
	Layer formation pressure:	0.2-0.9 Pa
	Target power:	1.0-2.0 kW
	Bias voltage:	Ground to -300 V

15 In this apparatus, the above nickel-phosphorus alloy plating layer was heat-treated (age hardening treatment) at  $250^{\circ}\text{C}$  for 30 minutes to obtain a watchband.

The obtained watchband had a surface hardness (HV: Vickers hardness, 25 g, impression time of 10 seconds) of 20 650.

Separately, another watchband was prepared in the same manner as above by forming a white-colored stainless steel coating layer in a thickness of  $2\mu\text{m}$ , and heat-treating the nickel-phosphorus alloy plating layer under 25 the same conditions as above.

The obtained watchband had a surface hardness (HV: Vickers hardness, 25 g, impression time of 10 seconds) of 650.

The resulting watchbands were tested for the corrosion resistance of the plating layer according to the aforementioned method. The rating numbers were not lower than 9.8, showing that the corrosion resistance was "good".

(Example 4)

A base article of a watchband was shaped from brass by machining. This base article was washed and degreased with an organic solvent.

The base article was immersed in a plating solution having the composition below. A copper-tin alloy plating layer was formed in a thickness of  $2\mu\text{m}$  on the base article surface by electroplating under the plating conditions below. The plated article was washed with water.

«Copper-Tin Alloy Plating»

(Plating Solution Composition)

Copper	15 g/lit.
Tin	15 g/lit.
Zinc	1 g/lit.
Potassium cyanide (free)	$30\pm 2$ g/lit.

(Plating Conditions)

pH	12.7
Solution temperature	50°C
Current density (Dk)	2 A/dm <sup>2</sup>
Layer forming rate	3 minutes/1μm

5 This watchband base article having the copper-tin alloy plating layer was immersed in a plating solution having the composition below. A copper-tin-palladium alloy plating layer was formed in a thickness of 2μm on the copper-tin alloy plating layer surface by

10 electroplating under the plating conditions below. The plated base article was washed with water.

«Copper-Tin-Palladium Alloy Plating»

〈Plating Solution Composition〉

Sodium stannate trihydrate ( $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ )

15 60 g/L (26.7 g/lit. in terms of Sn)

Copper cyanide ( $\text{CuCN}$ )

20 g/L (14.2 g/lit. in terms of Cu)

Palladium potassium cyanide hydrate ( $\text{K}_2\text{Pd}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$ )

30 g/L (9.3 g/lit. in terms of Pd)

20 Amidosulfonic acid ( $\text{NH}_2\text{SO}_3\text{H}$ ) 10 g/lit.

Potassium cyanide (free) 30 g/lit.

Potassium hydroxide 60 g/lit.

〈Plating Conditions〉

pH 12.5-13

25 Solution temperature 50-55°C

Current density (Dk)	2 A/dm <sup>2</sup>
Layer forming rate	0.33 μm/minute

This watchband base article having the copper-tin-palladium alloy plating layer was immersed in a plating solution having the composition below. A gold strike plating layer (flash plating) was formed in a thickness of 0.1-0.2 μm on the copper-tin-palladium alloy plating layer surface by electroplating under the plating conditions below. The plated base article was washed with water.

#### 10 «Gold Strike Plating»

##### 〈Plating Solution Composition〉

Gold	3-5 g/lit.
Sulfuric acid	10 g/lit.

##### 〈Plating Conditions〉

15 pH	1< (Specifically 0.3 to less than 1)
Solution temperature	25°C
Current density (Dk)	3-5 A/dm <sup>2</sup>
Time	30 seconds

20 This plated base article was set in a sputtering apparatus, and the surface of the base article was cleaned by bombard cleaning in an argon atmosphere.

On the surface of the gold strike plating layer formed on this base article, a white-colored stainless steel coating layer was formed in a thickness of 0.5 μm by 25 a sputtering method under the layer formation conditions

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&lt;Layer Formation Conditions&gt;

Sputtering gas: Argon gas

Target power: 1.0-2.0 kW

The resulting watchband was tested for the corrosion resistance of the plating layer according to the aforementioned method. The rating number was not lower than 9.8, showing that the corrosion resistance was "good".

A base article of a watchband was shaped from zinc  
15 by machining. This base article was washed and degreased  
with an organic solvent.

## 《Copper Plating》

25      Copper pyrophosphate      100 g/lit.

Potassium pyrophosphate	340 g/lit.
Ammonium citrate	10 g/lit.
Ammonia	3 g/lit.

〈Plating Conditions〉

5	pH	8.5
	Bath temperature	50°C
	Current density (Dk)	3 A/dm <sup>2</sup>

10 This base article having the copper plating layer was immersed in a plating solution having the composition below. A copper-tin alloy plating layer was formed in a thickness of 2  $\mu$ m on the above base article surface by electroplating under the plating conditions below. The plated base article was washed with water.

《Copper-Tin Alloy Plating》

15 〈Plating Solution Composition〉

Copper	15 g/lit.
Tin	15 g/lit.
Zinc	1 g/lit.
Potassium cyanide (free)	30 $\pm$ 2 g/lit.

20 〈Plating Conditions〉

pH	12.7
Solution temperature	50°C
Current density (Dk)	2 A/dm <sup>2</sup>
Layer forming rate	3 minutes/1 $\mu$ m

25 This watchband base article having the copper-tin



5 electroplating under the plating conditions below. The plated base article was washed with water.

(Plating Solution Composition)

10 60 g/lit. (26.7 g/lit. in terms of Sn)

20 g/lit. (14.2 g/lit. in terms of Cu)

30 g/lit. (9.3 g/lit. in terms of Pd)

Potassium cyanide (free) 30 g/lit.

(Plating Conditions)

20      Solution temperature      50-55°C

Layer forming rate 0.33  $\mu\text{m}/\text{minute}$

This watchband base article having the copper-tin-palladium alloy plating layer was immersed in a plating solution having the composition below. A palladium strike

plating layer (flash plating) was formed in a thickness of  $0.2\mu\text{m}$  on the copper-tin-palladium alloy plating layer surface by electroplating under the plating conditions below. The plated base article was washed with water.

# 5 《Palladium Strike Plating》

## 《Plating Solution Composition》

Pure palladium 1-3 g/lit.

## 《Plating Conditions》

pH 8

10 Solution temperature  $32^{\circ}\text{C}$

Current density (Dk) 3-5 A/dm<sup>2</sup>

Time 30 seconds

This plated base article was set in a sputtering apparatus, and the surface of the base article was cleaned  
15 by bombard cleaning in an argon atmosphere.

On the surface of the palladium strike plating layer formed on this base article, a white-colored stainless steel coating layer was formed in a thickness of  $1.0\mu\text{m}$  by a sputtering method under the layer formation  
20 conditions below to obtain a watchband.

## 《Layer Formation Conditions》

Target: Nickel-free ferritic stainless steel SUS444

Sputtering gas: Argon gas

Layer formation pressure: 0.2-0.9 Pa

25 Target power: 1.0-2.0 kW

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Bias voltage:

Ground to -300 V

The resulting watchband was tested for the corrosion resistance of the plating layer according to the aforementioned method. The rating number was not lower  
5 than 9.8, showing that the corrosion resistance was "good".

(Example 6)

A base article of a watchcase was shaped by machining from a zinc alloy (composition: Al, 3.5-4.3%; Cu,  
10 0.75-1.25%; Mg, 0.02-0.08%; and balance of Zn). This base article was washed and degreased with an organic solvent.

This watch case base article was immersed in a plating solution having the composition below. A copper plating layer was formed in a thickness of 8  $\mu$ m on the  
15 base article surface by electroplating under the plating conditions below. The plated article was washed with water.

«Copper Plating»

〈Plating Solution Composition〉

20	Copper pyrophosphate	100 g/lit.
	Potassium pyrophosphate	340 g/lit.
	Ammonium citrate	10 g/lit.
	Ammonia	3 g/lit.

〈Plating Conditions〉

25	pH	8.5
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Solution temperature	50°C
Current density (Dk)	3 A/dm <sup>2</sup>

This base article having the copper plating layer was immersed in a plating solution having the composition below. A copper-tin alloy plating layer was formed in a thickness of 2  $\mu$ m on base article surface by electroplating under the plating conditions below. The plated base article was washed with water.

《Copper-Tin Alloy Plating》

10 〈Plating Solution Composition〉

Copper	15 g/lit.
Tin	15 g/lit.
Zinc	1 g/lit.
Potassium cyanide (free)	30 $\pm$ 2 g/lit.

15 〈Plating Conditions〉

pH	12.7
Solution temperature	50°C
Current density (Dk)	2 A/dm <sup>2</sup>
Layer forming rate	3 minutes/1 $\mu$ m

20 This watch case base article having the copper-tin alloy coating layer was set in an ion plating apparatus, and the surface of the base article was cleaned by bombard cleaning in an argon atmosphere.

On the surface of the copper-tin alloy plating layer formed on this base article surface, a titanium

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carbide plating layer of a white color tone was formed in a thickness of  $0.2\mu\text{m}$  by an ion plating process (hot cathode method) under the layer formation conditions below.

(Layer Formation Conditions)

5	Evaporation source:	Titanium
	Gas:	Gas mixture of $\text{C}_2\text{H}_4$ , $\text{CH}_4$ and $\text{C}_6\text{H}_6$
	Layer formation pressure:	0.15-0.65 Pa
	Anode voltage:	40-60 V
	Bias voltage:	Ground to -200 V
10	Filament current:	50 A
	E/B:	10 kV, 0.25-0.35 mA

On the surface of the titanium carbide plating layer formed on this base article surface, a stainless steel coating layer of a white color tone was formed in a thickness of  $0.3\mu\text{m}$  by an ion plating process under the layer formation conditions below.

(Layer Formation Conditions)

	Evaporation source:	Nickel-free ferritic stainless steel SUS444
20	Gas:	Argon gas
	Layer formation pressure:	0.15-0.65 Pa
	Anode voltage:	40-50 V
	Bias voltage:	Ground to -200 V
	Filament current:	50 A
25	E/B:	10 kV, 0.2-0.3 mA

The resulting watchcase was tested for the corrosion resistance of the plating layer according to the aforementioned method. The rating number was not lower than 9.8, showing that the corrosion resistance was "good".

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(Example 7)

A base article of an earring was shaped by machining a magnesium alloy (composition: Al, 8.3-11.0%; Zn, 0.3-1.0%; Mn, 0.13-0.5%; and balance of Mg). This base article was washed and degreased with an organic solvent.

This earring base article was immersed in a plating solution having the composition below. A copper plating layer was formed in a thickness of  $8\mu\text{m}$  on the base article surface by electroplating under the plating conditions below. The plated article was washed with water.

#### «Copper Plating»

##### 〈Plating Solution Composition〉

20	Copper pyrophosphate	100 g/lit.
	Potassium pyrophosphate	340 g/lit.
	Ammonium citrate	10 g/lit.
	Ammonia	3 g/lit.

##### 〈Plating Conditions〉

25	pH	8.5
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Bath temperature	50°C
Current density (Dk)	3 A/dm <sup>2</sup>

This base article having the copper plating layer was immersed in a plating solution having the composition below. A copper-tin-palladium alloy plating layer was formed in a thickness of 2 μm on the base article surface by electroplating under the plating conditions below. The plated base article was washed with water.

《Copper-Tin-Palladium Alloy Plating》

10 〈Plating Solution Composition〉

Sodium stannate trihydrate (Na <sub>2</sub> SnO <sub>3</sub> · 3H <sub>2</sub> O)	
	60 g/L (26.7 g/lit. in terms of Sn)

Copper cyanide (CuCN)	
	20 g/L (14.2 g/lit. in terms of Cu)

15 Palladium potassium cyanide hydrate (K <sub>2</sub> Pd(CN) <sub>4</sub> · 3H <sub>2</sub> O)	
	30 g/lit. (9.3 g/lit. in terms of Pd)

Amidosulfonic acid (NH <sub>2</sub> SO <sub>3</sub> H)	10 g/L
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Potassium cyanide (free)	30 g/lit.
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Potassium hydroxide	60 g/lit.
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20 〈Plating Conditions〉

pH	12.5-13
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Solution temperature	50-55°C
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Current density (Dk)	2 A/dm <sup>2</sup>
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Layer forming rate	0.33 μm/minute
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25 This base article was set in an ion plating

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apparatus, and the surface of the base article was cleaned by bombard cleaning in an argon atmosphere.

On the surface of the copper-tin-palladium alloy plating layer formed on the base article surface, a stainless steel coating layer of a white color tone was formed in a thickness of  $1.2\mu\text{m}$  by an ion plating process under the layer formation conditions below to obtain an earring.

(Layer Formation Conditions)

10 Evaporation source:

Nickel-free ferritic stainless steel SUS444

Gas: Argon gas

Layer formation pressure: 0.15-0.65 Pa

Anode voltage: 40-50 V

15 Bias voltage: Ground to -200 V

Filament current: 50 A

E/B: 10 kV, 0.2-0.3 mA

The resulting earring was tested for the corrosion resistance of the plating layer according to the aforementioned method. The rating number was not lower than 9.8, showing that the corrosion resistance was "good".

(Example 8)

A base article of a necklace was shaped from brass by machining. This base article was washed and degreased



with an organic solvent.

This base article was immersed in a plating solution having the composition below. A nickel strike plating layer (flash plating) was formed in a thickness of 0.1-0.2  $\mu\text{m}$  on the base article surface by electroplating under the plating conditions below. The plated article was washed with water.

《Nickel Strike Plating》

〈Plating Solution Composition〉

10	Nickel chloride	180 g/lit.
	Hydrochloric acid	100 g/lit.

〈Plating Conditions〉

	pH	1< (specifically 0.3 to less than 1)
	Solution temperature	Room temperature
15	Current density (Dk)	3-5 A/dm <sup>2</sup>
	Time	30-60 seconds

This necklace article having a nickel strike plating layer was immersed in a plating solution having the composition below. A nickel plating layer was formed in a thickness of 4  $\mu\text{m}$  on the nickel strike plating layer surface by electroplating under the plating conditions below. The plated base article was washed with water.

《Nickel Plating》

〈Plating Solution Composition〉

25	Nickel sulfate	250 g/lit.
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Nickel chloride 75 g/lit.

Boric acid 50 g/lit.

Brightener (Brightener #61, produced by Ebara-Udylite Co., Ltd.)

5 0.5 ml/lit.

(Plating Conditions)

pH 3.6-4.0

Solution temperature 40-50°C

Current density (Dk) 3 A/dm<sup>2</sup>

10 This plated base article was set in a sputtering apparatus, and the surface of the base article was cleaned by bombard cleaning in an argon atmosphere.

On the surface of the nickel plating layer formed on this base article surface, a white-colored stainless steel coating layer was formed in a thickness of 1.0 μm by a sputtering method under the layer formation conditions below.

(Layer Formation Conditions)

Target: Austenitic stainless steel SUS304

20 Sputtering gas: Argon gas

Layer formation pressure: 0.2-0.9 Pa

Target power: 1.0-2.0 kW

Bias voltage: Ground to -300 V

On a prescribed portion of the surface of the stainless steel coating layer formed on the necklace base

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article surface, an organic masking agent composed of an epoxy type resin was applied to form a masking layer.

The necklace base article having the masking layer formed thereon was washed with isopropyl alcohol, and was set in a sputtering apparatus. A titanium nitride coating layer was formed in a thickness of  $0.2\mu\text{m}$  on the surface of the stainless steel coating layer and on the surface of the masking layer by sputtering under the layer formation conditions below.

10 (Layer formation conditions)

Target:	Titanium (Ti)
Sputtering gas:	Nitrogen gas
Layer formation pressure:	0.2-0.9 Pa
Target power:	1.0-2.0 kW
15 Bias voltage:	Ground to -300 V

The masking layer was swelled by immersion in a peeling solution composed of ethyl methyl ketone (EMK) containing formic acid and hydrogen peroxide. The masking layer with the titanium nitride coating layer was peeled off to obtain a necklace having an outermost coating layer (finished plating layer) of two-color tone of a white-colored stainless steel coating layer and a gold-colored titanium nitride coating layer.

The resulting necklace was tested for the corrosion resistance of the plating layer according to the

aforementioned method. The rating number was not lower than 9.8, showing that the corrosion resistance was "good".

(Example 9)

5           A base article of a watchband was shaped from brass by machining. This base article was washed and degreased with an organic solvent.

10           This base article was immersed in a plating solution having the composition below. A nickel strike plating layer (flash plating) was formed in a thickness of 0.1-0.2  $\mu\text{m}$  on the base article surface by electroplating under the plating conditions below. The plated article was washed with water.

《Nickel Strike Plating》

15   〈Plating Solution Composition〉

Nickel chloride                      180 g/lit.

Hydrochloric acid                    100 g/lit.

Brightener (Brightener #61, produced by Ebara-Udylite Co., Ltd.)

20                                      0.5 ml/lit.

〈Plating Conditions〉

pH                                    <1 (specifically, 0.3 to less than 1)

Solution temperature                Room temperature

Current density (Dk)                3-5 A/dm<sup>2</sup>

25   Time                              30-60 seconds

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This watchband base article having a nickel strike plating layer was immersed in a plating solution having the composition below. A nickel plating layer was formed in a thickness of  $2\mu\text{m}$  on the nickel strike plating layer surface by electroplating under the plating conditions below. The plated base article was washed with water.

《Nickel Plating》

〈Plating Solution Composition〉

Nickel sulfate 250 g/lit.

Nickel chloride 75 g/lit.

Boric acid 50 g/lit.

Brightener

(Brightener #61, produced by Ebara-Udylite Co., Ltd.)

0.5 ml/lit.

15 〈Plating Conditions〉

pH 3.6-4.0

Solution temperature 40-50°C

Current density (Dk) 3 A/dm<sup>2</sup>

This watchband base article having a nickel plating layer was immersed in a plating solution having the composition below. A nickel-phosphorus alloy plating layer was formed in a thickness of  $2\mu\text{m}$  on the nickel plating layer surface by electroplating under the plating conditions below. The plated base article was washed with water.

# 《Nickel-Phosphorus Alloy Plating》

## 〈Plating Solution Composition〉

	Nickel sulfate	40-50 g/lit.
	Nickel hydroxide	10-20 g/lit.
5	Sodium hypophosphite	3-10 g/lit.
	Phosphoric acid	10-20 ml/lit.
	Sodium citrate	30-50 g/lit.

## 〈Plating Conditions〉

	pH	2.6-3.2
10	Solution temperature	55°C
	Current density (Dk)	2 A/dm <sup>2</sup>

This watchband base article having a nickel-phosphorus alloy plating layer was immersed in a plating solution having the composition below. A palladium-nickel alloy plating layer (flash plating) was formed in a thickness of 0.1-0.2  $\mu$ m on the nickel-phosphorus plating layer surface by electroplating under the plating conditions below. The plated base article was washed with water, and dried.

# 20 《Palladium-Nickel Alloy Plating》

## 〈Plating Solution Composition〉

	Palladium	7.5 g/lit.
	Nickel	12.5 g/lit.

## 〈Plating Conditions〉

25	pH	8
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Solution temperature	32°C
Current density (Dk)	1.0 A/dm <sup>2</sup>
Specific gravity (Be)	12.5
Layer forming rate	4.2 minutes/1 μm

5 This plated base article was set in a sputtering apparatus, and the surface of the base article was cleaned by bombard cleaning in an argon atmosphere.

On the surface of the palladium-nickel alloy plating layer formed on this base article surface, a  
10 titanium plating layer was formed in a thickness of 0.2-0.5 μm by a sputtering method under the layer formation conditions below.

〈Layer Formation Conditions〉

15 Target:	Titanium
Sputtering gas:	Argon gas
Layer formation pressure:	0.2-0.9 Pa
Target power:	1.0-2.0 kW
Bias voltage:	Ground to -300 V

20 On the surface of the titanium plating layer formed on this base article surface, a titanium carbide plating layer was formed in a thickness of 0.4 μm by a sputtering method under the layer formation conditions below.

〈Layer Formation Conditions〉

25 Target:	Titanium
Sputtering gas:	Gas mixture of C <sub>2</sub> H <sub>4</sub> , CH <sub>4</sub> and C <sub>6</sub> H <sub>6</sub>

Layer formation pressure: 0.2-0.9 Pa  
 Target power: 1.0-2.0 kW  
 Bias voltage: Ground to -300 V

On the surface of the titanium carbide plating  
 5 layer formed on this base article surface, a white-colored  
 stainless steel coating layer was formed in a thickness of  
 0.3 $\mu$ m by a sputtering method under the layer formation  
 conditions below to obtain a watchband.

(Layer Formation Conditions)

10 Target: Austenitic stainless steel SUS304  
 Sputtering gas: Argon gas  
 Layer formation pressure: 0.2-0.9 Pa  
 Target power: 1.0-2.0 kW  
 Bias voltage: Ground to -300 V

15 The resulting watchband was tested for the  
 corrosion resistance of the plating layer according to the  
 aforementioned method. The rating numbers were not lower  
 than 9.8, showing that the corrosion resistance was "good".

20 (Example 10)

A watchband having a titanium plating layer, a  
 titanium carbide plating layer, and a white-colored  
 stainless steel coating layer of 0.3 $\mu$ m thick was produced  
 in the same manner as in Example 9 except that the  
 25 titanium plating layer, the titanium carbide plating layer,



and the stainless steel coating layer were formed by an arc evaporation method instead of the sputtering method. The layer formation conditions of the arc evaporation method were shown below.

5   〈Titanium Plating Layer Formation Conditions〉

Target:	Titanium
Gas:	Argon gas
Layer formation pressure:	1.0-3.0 Pa
Target current:	80-100 A
10   Bias voltage:	-50 to -200 V

   〈Titanium Carbide Plating Layer Formation Conditions〉

Target:	Titanium
Gas:	Gas mixture of CH <sub>4</sub> , C <sub>2</sub> H <sub>4</sub> and C <sub>6</sub> H <sub>6</sub>
Layer formation pressure:	1.0-3.0 Pa
15   Target current:	80-100 A
Bias voltage:	-50 to -200 V

   〈Stainless Steel Coating Layer Formation Conditions〉

Target:	Austenitic stainless steel SUS304
Gas:	Argon gas
20   Layer formation pressure:	1.0-3.0 Pa
Target current:	80-100 A
Bias voltage:	-50 to -200 V

   The resulting watchband was tested for the corrosion resistance of the plating layer according to the  
 25   aforementioned method. The rating numbers were not lower

than 9.8, showing that the corrosion resistance was "good".

(Example 11)

A watchband having a titanium plating layer, a  
 5 titanium carbide plating layer and a white-colored  
 stainless steel coating layer of  $0.3\mu\text{m}$  thick was produced  
 in the same manner as in Example 9 except that the  
 titanium plating layer, the titanium carbide plating layer,  
 and the stainless steel coating layer were formed by an  
 10 ion plating method instead of the sputtering method. The  
 layer formation conditions of the ion plating method were  
 shown below.

〈Titanium Plating Layer Formation Conditions〉

	Evaporation source:	Titanium
15	Gas:	Argon gas
	Layer formation pressure:	0.15-0.65 Pa
	Anode voltage:	40-50 V
	Bias voltage:	Ground to -200 V
	Filament current	50 A
20	E/B:	10 kV, 0.25-0.35 mA

〈Titanium Carbide Plating Layer Formation Conditions〉

	Evaporation source:	Titanium
	Gas:	Gas mixture of $\text{CH}_4$ , $\text{C}_2\text{H}_4$ and $\text{C}_6\text{H}_6$
	Layer formation pressure:	0.15-0.65 Pa
25	Anode voltage:	40-50 V

Bias voltage: Ground to -200 V  
 Filament current 50 A  
 E/B: 10 kV, 0.25-0.35 mA

(Stainless Steel Coating Layer Formation Conditions)

5 Evaporation source:

Austenitic stainless steel SUS304

Gas: Argon gas  
 Layer formation pressure: 0.15-0.65 Pa  
 Anode voltage: 40-50 V  
 10 Bias voltage: Ground to -200 V  
 Filament current 50 A  
 E/B: 10 kV, 0.2-0.3 mA

The resulting watchband was tested for the corrosion resistance of the plating layer according to the  
 15 aforementioned method. The rating numbers were not lower than 9.8, showing that the corrosion resistance was "good".

(Example 12)

A base article of a watchcase was shaped from brass  
 20 by machining. This base article was washed and degreased with an organic solvent.

This base article was immersed in a plating solution having the composition below. A nickel strike plating layer (flash plating) was formed in a thickness of  
 25 0.1-0.2  $\mu\text{m}$  on the base article surface by electroplating

under the plating conditions below. The plated article was washed with water.

《Nickel Strike Plating》

〈Plating Solution Composition〉

5	Nickel chloride	180 g/lit.
	Hydrochloric acid	100 g/lit.

〈Plating Conditions〉

	pH	<1 (specifically, 0.3 to less than 1)
	Solution temperature	Room temperature
10	Current density (Dk)	3-5 A/dm <sup>2</sup>
	Time	30-60 seconds

This watchcase base article having a nickel strike plating layer was immersed in a plating solution having the composition below. A nickel plating layer was formed in a thickness of 2  $\mu$ m on the nickel strike plating layer surface by electroplating under the plating conditions below. The plated base article was washed with water.

《Nickel Plating》

〈Plating Solution Composition〉

20	Nickel sulfate	250 g/lit.
	Nickel chloride	75 g/lit.
	Boric acid	50 g/lit.
	Brightener	

(Brightener #61, produced by Ebara-Udylite Co., Ltd.)

25 0.5 ml/lit.

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(Plating Conditions)

pH	3.6-4.0
Solution temperature	40-50°C
Current density (Dk)	3 A/dm <sup>2</sup>

5           This watchcase base article having a nickel plating layer was immersed in a plating solution having the composition below. A nickel-phosphorus alloy plating layer was formed in a thickness of 2 μm on the nickel plating layer surface by electroplating under the plating conditions below. The plated base article was washed with water.

«Nickel-Phosphorus Alloy Plating»

(Plating Solution Composition)

Nickel sulfate	40-50 g/lit.
15   Nickel hydroxide	10-20 g/lit.
Sodium hypophosphite	3-10 g/lit.
Phosphoric acid	10-40 ml/lit.
Sodium citrate	30-50 g/lit.

(Plating Conditions)

20   pH	2.6-3.2
Solution temperature	55°C
Current density (Dk)	2 A/dm <sup>2</sup>

          This watchcase base article having a nickel-phosphorus alloy plating layer was immersed in a plating solution having the composition below. A palladium-nickel

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alloy plating layer (flash plating) was formed in a thickness of 0.1-0.2  $\mu\text{m}$  on the nickel-phosphorus alloy plating layer surface by electroplating under the plating conditions below. The plated base article was washed with water, and dried.

# 《Palladium-Nickel Alloy Plating》

## 〈Plating Solution Composition〉

Palladium	7.5 g/lit.
Nickel	12.5 g/lit.

## 10 〈Plating Conditions〉

pH	8
Solution temperature	32°C
Current density (Dk)	1.0 A/dm <sup>2</sup>
Specific gravity (Be)	12.5
15 Layer forming rate	4.2 minutes/1 $\mu\text{m}$

This plated base article was set in a sputtering apparatus, and the surface of the base article was cleaned by bombard cleaning in an argon atmosphere.

On the surface of the palladium-nickel alloy plating layer formed on this base article surface, a titanium plating layer was formed in a thickness of 0.2-0.5  $\mu\text{m}$  by a sputtering method under the layer formation conditions below.

## 〈Layer Formation Conditions〉

25 Target: Titanium

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Sputtering gas: Argon gas  
Layer formation pressure: 0.2-0.9 Pa  
Target power: 1.0-2.0 kW  
Bias voltage: Ground to -300 V

5 On the surface of the titanium plating layer formed on this base article surface, a white-colored stainless steel coating layer was formed in a thickness of  $0.3\mu\text{m}$  by a sputtering method under the layer formation conditions below to obtain a watchcase.

10 (Layer Formation Conditions)

Target: Austenitic stainless steel SUS304  
Sputtering gas: Argon gas  
Layer formation pressure: 0.2-0.9 Pa  
Target power: 1.0-2.0 kW  
15 Bias voltage: Ground to -300 V

The resulting watchcase was tested for the corrosion resistance of the plating layer according to the aforementioned method. The rating numbers were not lower than 9.8, showing that the corrosion resistance was "good".

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(Example 13)

A watchcase having a titanium plating layer and a white-colored stainless steel coating layer of  $0.3\mu\text{m}$  thick was produced in the same manner as in Example 12  
25 except that the titanium plating layer and the stainless

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steel coating layer were formed by an arc evaporation method instead of the sputtering method. The layer formation conditions of the arc evaporation method were shown below.

5   〈Titanium Plating Layer Formation Conditions〉

Target:	Titanium
Gas:	Argon gas
Layer formation pressure:	1.0-3.0 Pa
Target current:	80-100 A
10   Bias voltage:	-50 to -200 V

      〈Stainless Steel Coating Layer Formation Conditions〉

Target:	Austenitic stainless steel SUS304
Gas:	Argon gas
Layer formation pressure:	1.0-3.0 Pa
15   Target current:	80-100 A
Bias voltage:	-50 to -200 V

The resulting watchcase was tested for the corrosion resistance of the plating layer according to the aforementioned method. The rating numbers were not lower  
20 than 9.8, showing that the corrosion resistance was "good".

(Example 14)

A watchcase having a titanium plating layer, and a white-colored stainless steel coating layer of  $0.3\mu\text{m}$   
25 thick was produced in the same manner as in Example 12



except that the titanium plating layer and the stainless steel coating layer were formed by an ion plating process instead of the sputtering method. The layer formation conditions of the ion plating method were shown below.

5    〈Titanium Plating Layer Formation Conditions〉

Evaporation source:	Titanium
Gas:	Argon gas
Layer formation pressure:	0.15-0.65 Pa
Anode voltage:	40-60 V
10    Bias voltage:	Ground to -200 V
Filament current	50 A
E/B:	10 kV, 0.25-0.35 mA

   〈Stainless Steel Coating Layer Formation Conditions〉

15    Evaporation source:	Austenitic stainless steel SUS304
Gas:	Argon gas
Layer formation pressure:	0.15-0.65 Pa
Anode voltage:	40-50 V
Bias voltage:	Ground to -200 V
20    Filament current	50 A
E/B:	10 kV, 0.2-0.3 mA

   The resulting watchcase was tested for the corrosion resistance of the plating layer according to the aforementioned method. The rating numbers were not lower than 9.8, showing that the corrosion resistance was "good".

(Example 15)

A base article of a watchband was shaped from zinc by machining. This base article was washed and degreased with an organic solvent.

This watchband base article was immersed in a plating solution having the composition below. A copper-tin alloy plating layer was formed in a thickness of  $2\mu\text{m}$  on the surface of the base article by electroplating under the plating conditions below. The plated article was washed with water.

«Copper-Tin Alloy Plating»

〈Plating Solution Composition〉

	Copper	15 g/lit.
15	Tin	15 g/lit.
	Zinc	1 g/lit.
	Potassium cyanide (free)	$30\pm 2$ g/lit.

〈Plating Conditions〉

	pH	12.7
20	Solution temperature	$50^{\circ}\text{C}$
	Current density (Dk)	$2\text{ A/dm}^2$
	Layer forming rate	3 minutes/ $1\mu\text{m}$

This watchband base article having the copper-tin alloy plating layer was immersed in a plating solution having the composition below. A copper-tin-palladium

alloy plating layer was formed in a thickness of  $2\mu\text{m}$  on the copper-tin alloy plating layer surface by electroplating under the plating conditions below. The plated base article was washed with water.

# 5 «Copper-Tin-Palladium Alloy Plating»

## 〈Plating Solution Composition〉

Sodium stannate trihydrate ( $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ )

60 g/lit. (26.7 g/lit. in terms of Sn)

Copper cyanide 20 g/lit. (14.2 g/lit. in terms of Cu)

10 Palladium potassium cyanide hydrate ( $\text{K}_2\text{Pd}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$ )

30 g/lit. (9.3 g/lit. in terms of Pd)

Amidosulfonic acid ( $\text{NH}_2\text{SO}_2\text{H}$ ) 10 g/lit.

Potassium cyanide (free) 30 g/lit.

Potassium hydroxide 60 g/lit.

# 15 〈Plating Conditions〉

pH 12.5-13

Solution temperature 50-55°C

Current density (Dk) 2 A/dm<sup>2</sup>

Layer forming rate 0.33  $\mu\text{m}$ /minute

20 This watchband base article having the copper-tin-palladium alloy plating layer was immersed in a plating solution having the composition below. A palladium strike plating layer (flash plating) was formed in a thickness of  $0.2\mu\text{m}$  on the copper-tin-palladium alloy plating layer

25 surface by electroplating under the plating conditions

below. The plated base article was washed with water.

《Palladium Strike Plating》

〈Plating Solution Composition〉

Pure palladium 1-3 g/lit.

5 〈Plating Conditions〉

pH 8

Solution temperature 32°C

Current density (Dk) 3-5 A/dm<sup>2</sup>

Time 30 seconds

10 This plated base article was set in a sputtering apparatus, and the surface of the base article was cleaned by bombard cleaning in an argon atmosphere.

On the surface of the palladium strike plating layer formed on this base article, a titanium plating  
15 layer was formed in a thickness of 0.2-0.5 μm by a sputtering method under the layer formation conditions below.

〈Layer Formation Conditions〉

20 Target: Titanium  
Sputtering gas: Argon gas  
Layer formation pressure: 0.2-0.9 Pa  
Target power: 1.0-2.0 kW  
Bias voltage: Ground to -300 V

On the surface of the titanium plating layer formed  
25 on this base article surface, a titanium carbide plating

layer was formed in a thickness of  $0.4\mu\text{m}$  by a sputtering method under the layer formation conditions below.

〈Layer Formation Conditions〉

Target: Titanium

5 Sputtering gas: Gas mixture of  $\text{C}_2\text{H}_4$ ,  $\text{CH}_4$  and  $\text{C}_6\text{H}_6$

Layer formation pressure:  $0.2\text{--}0.9\text{ Pa}$

Target power:  $1.0\text{--}2.0\text{ kW}$

Bias voltage: Ground to  $-300\text{ V}$

10 On the surface of the titanium carbide plating layer formed on this base article, a white-colored stainless steel coating layer was formed in a thickness of  $0.5\mu\text{m}$  by a sputtering method under the layer formation conditions below to obtain a watchband.

〈Layer Formation Conditions〉

15 Target: Nickel-free ferritic stainless steel SUS444

Sputtering gas: Argon gas

Layer formation pressure:  $0.2\text{--}0.9\text{ Pa}$

Target power:  $1.0\text{--}2.0\text{ kW}$

Bias voltage: Ground to  $-300\text{ V}$

20 The resulting watchband was tested for the corrosion resistance of the plating layer according to the aforementioned method. The rating number was not lower than 9.8, showing that the corrosion resistance was "good".

25 (Example 16)

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A watchband having a titanium plating layer, a titanium carbide plating layer, and a white-colored stainless steel coating layer of  $0.5\mu\text{m}$  thick was produced in the same manner as in Example 15 except that the

5 titanium plating layer, the titanium carbide plating layer, and the stainless steel coating layer were formed by an arc evaporation method instead of the sputtering method. The layer formation conditions of the arc evaporation method were shown below.

10 <Titanium Plating Layer Formation Conditions>

Target:	Titanium
Gas:	Argon gas
Layer formation pressure:	1.0-3.0 Pa
Target current:	80-100 A
15 Bias voltage:	-50 to -200 V

<Titanium Carbide Plating Layer Formation Conditions>

Target:	Titanium
Gas:	Gas mixture of $\text{C}_2\text{H}_4$ , $\text{CH}_4$ and $\text{C}_6\text{H}_6$
Layer formation pressure:	1.0-3.0 Pa
20 Target current:	80-100 A
Bias voltage:	-50 to -200 V

<Stainless Steel Coating Layer Formation Conditions>

Target:	Nickel-free ferritic stainless steel SUS444
Gas:	Argon gas
25 Layer formation pressure:	1.0-3.0 Pa

Target current: 80-100 A  
 Bias voltage: -50 to -200 V

The resulting watchband was tested for the corrosion resistance of the plating layer according to the  
 5 aforementioned method. The rating numbers were not lower than 9.8, showing that the corrosion resistance was "good".

(Example 17)

A watchband having a titanium plating layer, a  
 10 titanium carbide plating layer and a white-colored stainless steel coating layer of  $0.5\mu\text{m}$  thick was produced in the same manner as in Example 15 except that the titanium plating layer, the titanium carbide plating layer and the stainless steel coating layer were formed by an  
 15 ion plating method instead of the sputtering method. The layer formation conditions of the ion plating method were as shown below.

〈Titanium Plating Layer Formation Conditions〉

Evaporation source:	Titanium
20 Gas:	Argon gas
Layer formation pressure:	0.15-0.65 Pa
Anode voltage:	40-60 V
Bias voltage:	Ground to -200 V
Filament current	50 A
25 E/B:	10 kV, 0.25-0.35 mA

〈Titanium Carbide Plating Layer Formation Conditions〉

Evaporation source: Titanium

Gas: Gas mixture of  $C_2H_4$ ,  $CH_4$  and  $C_6H_6$

Layer formation pressure: 0.15-0.65 Pa

5 Anode voltage: 40-60 V

Bias voltage: Ground to -200 V

Filament current 50 A

E/B: 10 kV, 0.25-0.35 mA

〈Stainless Steel Coating Layer Formation Conditions〉

10 Evaporation source:

Nickel-free ferritic stainless steel SUS444

Gas: Argon gas

Layer formation pressure: 0.15-0.65 Pa

Anode voltage: 40-50 V

15 Bias voltage: Ground to -200 V

Filament current 50 A

E/B: 10 kV, 0.2-0.3 mA

The resulting watchband was tested for the corrosion resistance of the plating layer according to the

20 aforementioned method. The rating numbers were not lower than 9.8, showing that the corrosion resistance was "good".

(Example 18)

A base article of a watchcase was shaped from zinc

25 by machining. This base article was washed and degreased



with an organic solvent.

This watchcase base article was immersed in a plating solution having the composition below. A copper-tin alloy plating layer was formed in a thickness of  $2\mu\text{m}$  on the base article surface by electroplating under the plating conditions below. The plated article was washed with water.

«Copper-Tin Alloy Plating»

〈Plating Solution Composition〉

10	Copper	15 g/lit.
	Tin	15 g/lit.
	Zinc	1 g/lit.
	Potassium cyanide (free)	$30\pm 2$ g/lit.

〈Plating Conditions〉

15	pH	12.7
	Solution temperature	$50^{\circ}\text{C}$
	Current density (Dk)	$2\text{ A/dm}^2$
	Layer forming rate	3 minutes/ $1\mu\text{m}$

This watchcase base article having the copper-tin alloy plating layer was immersed in a plating solution having the composition below. A copper-tin-palladium alloy plating layer was formed in a thickness of  $2\mu\text{m}$  on the copper-tin alloy plating layer surface by electroplating under the plating conditions below. The plated base article was washed with water.

(Plating Solution Composition)

5      Copper cyanide      20 g/lit. (14.2 g/lit. in terms of Cu)  
Palladium potassium cyanide hydrate ( $K_2Pd(CN)_4 \cdot 3H_2O$ )  
30 g/lit. (9.3 g/lit. in terms of Pd)

Potassium cyanide (free)	30 g/lit.
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(Plating Conditions)

Solution temperature 50-55°C

15	Layer forming rate	0.33 $\mu\text{m}/\text{minute}$
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This watchcase base article having the copper-tin-palladium alloy plating layer was immersed in a plating solution having the composition below. A gold strike plating layer (flash plating) was formed in a thickness of 0.1-0.2  $\mu$ m on the copper-tin-palladium alloy plating layer surface by electroplating under the plating conditions below. The plated base article was washed with water.

(Plating Solution Composition)

25 Gold 3-5 g/lit.

Sulfuric acid 10 g/lit.

〈Plating Conditions〉

pH <1 (specifically, 0.3 to less than 1.0)  
 Solution temperature 20-35°C  
 5 Current density (Dk) 3-5 A/dm<sup>2</sup>  
 Time 30 seconds

This plated base article was set in a sputtering apparatus, and the surface of the base article was cleaned by bombard cleaning in an argon atmosphere.

10 On the surface of the gold strike plating layer formed on this base article surface, a titanium plating layer was formed in a thickness of 0.2-0.5  $\mu$ m by a sputtering method under the layer formation conditions below.

15 〈Layer Formation Conditions〉

Target: Titanium  
 Sputtering gas: Argon gas  
 Layer formation pressure: 0.2-0.9 Pa  
 Target power: 1.0-2.0 kW  
 20 Bias voltage: Ground to -300 V

On the surface of the titanium plating layer formed on this base article surface, a white-colored stainless steel coating layer was formed in a thickness of 0.3  $\mu$ m by a sputtering method under the layer formation conditions  
 25 below to obtain a watchcase.

<Layer Formation Conditions>

Target: Nickel-free ferritic stainless steel SUS444

Sputtering gas: Argon gas

Layer formation pressure: 0.2-0.9 Pa

5 Target power: 1.0-2.0 kW

Bias voltage: Ground to -300 V

The resulting watchcase was tested for the corrosion resistance of the plating layer according to the  
aforementioned method. The rating number was not lower  
10 than 9.8, showing that the corrosion resistance was "good".

(Example 19)

A watchcase having a titanium plating layer and a  
white-colored stainless steel coating layer of  $0.3\mu\text{m}$   
15 thick was produced in the same manner as in Example 18  
except that the titanium plating layer and the stainless  
steel coating layer were formed by an arc evaporation  
method instead of the sputtering method. The layer  
formation conditions of the arc evaporation method were  
20 shown below.

<Titanium Coating Layer Formation Conditions>

Target: Titanium

Gas: Argon gas

Layer formation pressure: 1.0-3.0 Pa

25 Target current: 80-100 A

Bias voltage: -50 to -200 V

〈Stainless Steel Coating Layer Formation Conditions〉

Target: Nickel-free ferritic stainless steel SUS444

Gas: Argon gas

5 Layer formation pressure: 1.0-3.0 Pa

Target current: 80-100 A

Bias voltage: -50 to -200 V

10 The resulting watchcase was tested for the corrosion resistance of the plating layer according to the aforementioned method. The rating numbers were not lower than 9.8, showing that the corrosion resistance was "good".

(Example 20)

15 A watchcase having a titanium plating layer, and a white-colored stainless steel coating layer of  $0.3\mu\text{m}$  thick was produced in the same manner as in Example 18 except that the titanium plating layer and the stainless steel coating layer of Example 18 were formed by an ion plating method instead of the sputtering method. The layer formation conditions of the ion plating method were  
20 shown below.

〈Titanium Plating Layer Formation Conditions〉

Evaporation source: Titanium

Gas: Argon gas

Layer formation pressure: 0.15-0.65 Pa

25 Anode voltage: 40-60 V

Bias voltage: Ground to -200 V  
 Filament current 50 A  
 E/B: 10 kV, 0.25-0.35 mA

<Stainless Steel Coating Layer Formation Conditions>

5 Evaporation source:

Nickel-free ferritic stainless steel SUS444

Gas: Argon gas  
 Layer formation pressure: 0.15-0.65 Pa  
 Anode voltage: 40-50 V  
 10 Bias voltage: Ground to -200 V  
 Filament current 50 A  
 E/B: 10 kV, 0.2-0.3 mA

The resulting watchcase was tested for the corrosion resistance of the plating layer according to the  
 15 aforementioned method. The rating numbers were not lower than 9.8, showing that the corrosion resistance was "good".

(Example 21)

A base article of a watchband was shaped from brass  
 20 by machining. This base article was washed and degreased with an organic solvent.

The base article was immersed in a plating solution having the composition below. A copper-tin alloy plating layer (alloy metal ratio: Cu, 75 wt%; Sn, 20 wt%; and Zn,  
 25 5 wt%) was formed in a thickness of  $3\mu\text{m}$  on the base

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article surface by electroplating under the plating conditions below. The plated article was washed with water. Incidentally, the copper-tin alloy plating layer generally includes those containing zinc in a small amount.

# 5 《Copper-Tin Alloy Plating》

## 〈Plating Solution Composition〉

	Copper cyanide	15 g/lit. (in terms of Cu)
	Sodium stannate	15 g/lit. (in terms of Sn)
	Zinc cyanide	1 g/lit. (in terms of Zn)
10	KOH	20 g/lit.
	KCN (free)	30 g/lit.
	Brightener B (trade name)	10 ml/lit.

(produced by Nippon Shin-Kinzoku K.K.)

## 〈Plating Conditions〉

15	pH	12.5 (at 50°C)
	Solution temperature	50°C
	Current density (Dk)	2.0 A/dm <sup>2</sup>
	Electrolysis time	12 minutes
	Stirring of plating solution	Rotation of rack of
20	cathode rocker type	

This watchband base article having the copper-tin alloy plating layer was immersed in a plating solution having the composition below. A copper-tin-zinc alloy plating layer (alloy metal ratio: Cu, 50 wt%; Sn, 35 wt%;  
25 and Zn, 15 wt%) was formed in a thickness of 2.5 μm on the

copper-tin alloy plating layer surface by electroplating under the plating conditions below. The plated base article was washed with water.

《Copper-Tin-Zinc Alloy Plating》

5 〈Plating Solution Composition〉

Copper cyanide	8.5 g/lit.(in terms of Cu)
Sodium stannate	34.0 g/lit.(in terms of Sn)
Zinc cyanide	1.0 g/lit.(in terms of Zn)
KOH	20 g/lit.
10 KCN (free)	50 g/lit.
Brightener 1-1 (trade name)	0.5 ml/lit.
	(produced by Degussa Japan Co., Ltd.)
Brightener 2 (trade name)	0.5 ml/lit.
	(produced by Degussa Japan Co., Ltd.)

15 〈Plating Conditions〉

pH	13.0 (at 60°C)
Solution temperature	60.0°C
Current density (Dk)	2.0 A/dm <sup>2</sup>
Electrolysis time	15 minutes

20 This watchband base article having the copper-tin-zinc alloy plating layer was immersed in a plating solution having the composition below. A gold strike plating layer (flash plating) was formed in a thickness of 0.1-0.2  $\mu$ m on the copper-tin-zinc alloy plating layer

25 surface by electroplating under the plating conditions



below. The plated base article was washed with water.

《Gold Strike Plating》

〈Plating Solution Composition〉

Auric potassium cyanide ( $\text{KAu}(\text{CN})_4$ )

5 2.0 g/lit. (in terms of Au)

Sulfuric acid (aqueous 10% solution) 10 g/lit.

〈Plating Conditions〉

pH 0.3 to 1

Solution temperature Room temperature

10 Current density (Dk) 3 A/dm<sup>2</sup>

Electrolysis time 15 seconds

This plated base article was set in a sputtering apparatus, and the surface of the base article was cleaned by bombard cleaning in an argon atmosphere.

15 On the surface of the gold strike plating layer formed on this base article surface, a white-colored stainless steel coating layer was formed in a thickness of 0.5  $\mu\text{m}$  by a sputtering method under the layer formation conditions below to obtain a watchband.

20 〈Layer Formation Conditions〉

Target: Austenitic stainless steel SUS310S

Sputtering gas: Argon gas

Layer formation pressure: 0.2-0.9 Pa

Target power: 1.0-2.0 kW

25 Bias voltage: Ground to -300 V

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The resulting watchband was tested for the corrosion resistance of the plating layer according to the aforementioned method. The rating number was not lower than 9.8, showing that the corrosion resistance was "good".

5

(Example 22)

A base article of a watchband was shaped from zinc by machining. This base article was washed and degreased with an organic solvent.

10

This base article was immersed in a plating solution having the composition below. A copper plating layer was formed in a thickness of  $8\mu\text{m}$  on the base article surface by electroplating under the plating conditions below. The plated article was washed with

15 water.

《Copper Plating》

〈Plating Solution Composition〉

Copper pyrophosphate 100 g/lit.

Potassium pyrophosphate 340 g/lit.

20 Ammonium citrate 10 g/lit.

Ammonia 3 g/lit.

〈Plating Conditions〉

pH 8.5

Solution temperature  $50^{\circ}\text{C}$

25 Current density (Dk)  $3\text{ A/dm}^2$ 

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This base article having a copper-plating layer was immersed in a plating solution having the composition below. A copper-tin alloy plating layer (alloy metal ratio: Cu, 75 wt%; Sn, 20 wt%; and Zn, 5 wt%) was formed in a thickness of  $3\mu\text{m}$  on the base article surface by electroplating under the plating conditions below. The plated article was washed with water.

«Copper-Tin Alloy Plating»

〈Plating Solution Composition〉

10	Copper cyanide	15 g/lit. (in terms of Cu)
	Sodium stannate	15 g/lit. (in terms of Sn)
	Zinc cyanide	1 g/lit. (in terms of Zn)
	KOH	20 g/lit.
	KCN (free)	30 g/lit.
15	Brightener B (trade name)	10 ml/lit.

(produced by Nippon Shin-Kinzoku K.K.)

〈Plating Conditions〉

	pH	12.5 (at $50^{\circ}\text{C}$ )
	Solution temperature	$50^{\circ}\text{C}$
20	Current density (Dk)	$2.0 \text{ A/dm}^2$
	Electrolysis time	12 minutes
	Stirring of plating solution	Rotation of rack of cathode rocker type

This watchband base article having the copper-tin alloy plating layer was immersed in a plating solution

having the composition below. A copper-tin-zinc alloy plating layer (alloy metal ratio: Cu, 50 wt%; Sn, 35 wt%; and Zn, 15 wt%) was formed in a thickness of  $2.5\mu\text{m}$  on the copper-tin alloy plating layer surface by electroplating under the plating conditions below. The plated base article was washed with water.

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## 《Copper-Tin-Zinc Alloy Plating》

### 〈Plating Solution Composition〉

	Copper cyanide	8.5 g/lit.(in terms of Cu)
10	Sodium stannate	34.0 g/lit.(in terms of Sn)
	Zinc cyanide	1.0 g/lit.(in terms of Zn)
	KOH	20 g/lit.
	KCN (free)	50 g/lit.
	Brightener 1-1 (trade name)	0.5 ml/lit.
15	(produced by Degussa Japan Co., Ltd.)	
	Brightener 2 (trade name)	0.5 ml/lit.
	(produced by Degussa Japan Co., Ltd.)	

### 〈Plating Conditions〉

	pH	13.0 (at 60°C)
20	Solution temperature	60.0°C
	Current density (Dk)	2.0 A/dm <sup>2</sup>
	Electrolysis time	15 minutes

This watchband base article having the copper-tin-zinc alloy plating layer was immersed in a plating solution having the composition below. A palladium strike

plating layer (flash plating) was formed in a thickness of  $0.2\mu\text{m}$  on the copper-tin-zinc alloy plating layer surface by electroplating under the plating conditions below. The plated base article was washed with water.

5 «Palladium Strike Plating»

⟨Plating Solution Composition⟩

Pure palladium 1-3 g/lit.

⟨Plating Conditions⟩

pH 8

10 Solution temperature  $32^{\circ}\text{C}$

Current density (Dk)  $3-5\text{ A/dm}^2$

Time 30 seconds

This plated base article was set in a sputtering apparatus, and the surface of the base article was cleaned  
15 by bombard cleaning in an argon atmosphere.

On the surface of the palladium strike plating layer formed on this base article, a white-colored stainless steel coating layer was formed in a thickness of  $1.0\mu\text{m}$  by a sputtering method under the layer formation  
20 conditions below to obtain a watchband.

⟨Layer Formation Conditions⟩

Target: Austenitic stainless steel SUS310S

Sputtering gas: Argon gas

Layer formation pressure:  $0.2-0.9\text{ Pa}$

25 Target power:  $1.0-2.0\text{ kW}$

Bias voltage:

Ground to -300 V

The resulting watchband was tested for the corrosion resistance of the plating layer according to the aforementioned method. The rating number was not lower  
5 than 9.8, showing that the corrosion resistance was "good".

(Example 23)

A base article of an earring was prepared by machining a magnesium alloy (composition: Al, 8.3-11.0%;  
10 Zn, 0.3-1.0%; Mn, 0.13-0.5%; and balance of Mg). This base article was washed and degreased with an organic solvent.

This earring base article was immersed in a plating solution having the composition below. A copper plating  
15 layer was formed in a thickness of  $8\mu\text{m}$  on the base article surface by electroplating under the plating conditions below. The plated article was washed with water.

«Copper Plating»

20 <Plating Solution Composition>

Copper pyrophosphate	100 g/lit.
Potassium pyrophosphate	340 g/lit.
Ammonium citrate	10 g/lit.
Ammonia	3 g/lit.

25 <Plating Conditions>

pH	8.5
Solution temperature	50°C
Current density (Dk)	3 A/dm <sup>2</sup>

This base article having the copper plating layer  
 5 was immersed in a plating solution having the composition  
 below. A copper-tin-zinc alloy plating layer (alloy metal  
 ratio: Cu, 50 wt%; Sn, 35 wt%; and Zn, 15 wt%) was formed  
 in a thickness of 2.5  $\mu$ m on the base article surface by  
 electroplating under the plating conditions below. The  
 10 plated base article was washed with water.

«Copper-Tin-Zinc Alloy Plating»

〈Plating Solution Composition〉

Copper cyanide 8.5 g/lit. (in terms of Cu)

Sodium stannate 34.0 g/lit. (in terms of Sn)

15 Zinc cyanide 1.0 g/lit. (in terms of Zn)

KOH 20 g/lit.

KCN (free) 50 g/lit.

Brightener 1-1 (trade name) 0.5 ml/lit.

(produced by Degussa Japan Co., Ltd.)

20 Brightener 2 (trade name) 0.5 ml/lit.

(produced by Degussa Japan Co., Ltd.)

〈Plating Conditions〉

pH 13.0 (at 60°C)

Solution temperature 60.0°C

25 Current density (Dk) 2.0 A/dm<sup>2</sup>

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Electrolysis time 15 minutes

This plated base article was set in an ion plating system, and the surface of the base article was cleaned by bombard cleaning in an argon atmosphere.

5 On the surface of the copper-tin-zinc alloy plating layer formed on this base article surface, a white-colored stainless steel coating layer was formed in a thickness of  $1.2\mu\text{m}$  by a sputtering method under the layer formation conditions below to obtain an earring.

10 (Layer Formation Conditions)

Evaporation source: Austenitic stainless steel SUS310S

Gas: Argon gas

Layer formation pressure: 0.2-0.9 Pa

Target power: 1.0-2.0 kW

15 Bias voltage: Ground to -300 V

The resulting earring was tested for the corrosion resistance of the plating layer according to the aforementioned method. The rating number was not lower than 9.8, showing that the corrosion resistance was "good".

20

(Example 24)

A base article of a watchband was shaped from brass by machining. This base article was washed and degreased with an organic solvent.

25 The watchband base article was immersed in a



plating solution having the composition below. A copper-tin alloy plating layer (alloy metal ratio: Cu, 75 wt%; Sn, 20 wt%; and Zn, 5 wt%) was formed in a thickness of  $3\mu\text{m}$  on the base article by electroplating under the plating conditions below. The plated article was washed with water.

《Copper-Tin Alloy Plating》

〈Plating Solution Composition〉

	Copper cyanide	15 g/lit. (in terms of Cu)
10	Sodium stannate	15 g/lit. (in terms of Sn)
	Zinc cyanide	1 g/lit. (in terms of Zn)
	KOH	20 g/lit.
	KCN (free)	30 g/lit.
	Brightener B (trade name)	10 ml/lit.
15	(produced by Nippon Shin-Kinzoku K.K.)	

〈Plating Conditions〉

	pH	12.5 (at $50^{\circ}\text{C}$ )
	Solution temperature	$50^{\circ}\text{C}$
	Current density (Dk)	$2.0 \text{ A/dm}^2$
20	Electrolysis time	12 minutes
	Stirring of plating solution    Rotation of rack of cathode rocker type	

This watchband base article having the copper-tin alloy plating layer was immersed in a plating solution having the composition below. A copper-tin-zinc alloy

plating layer (alloy metal ratio: Cu, 50 wt%; Sn, 35 wt%, and Zn, 15 wt%) was formed in a thickness of  $2.5\mu\text{m}$  on the copper-tin alloy plating layer surface by electroplating under the plating conditions below. The plated base

5 article was washed with water.

### 《Copper-Tin-Zinc Alloy Plating》

#### 〈Plating Solution Composition〉

	Copper cyanide	8.5 g/lit. (in terms of Cu)
	Sodium stannate	34.0 g/lit. (in terms of Sn)
10	Zinc cyanide	1.0 g/lit. (in terms of Zn)
	KOH	20 g/lit.
	KCN (free)	50 g/lit.
	Brightener 1-1 (trade name)	0.5 ml/lit.
	(produced by Degussa Japan Co., Ltd.)	
15	Brightener 2 (trade name)	0.5 ml/lit.
	(produced by Degussa Japan Co., Ltd.)	

#### 〈Plating Conditions〉

	pH	13.0 (at $60^{\circ}\text{C}$ )
	Solution temperature	$60.0^{\circ}\text{C}$
20	Current density (Dk)	$2.0\text{ A/dm}^2$
	Electrolysis time	15 minutes

This watchband base article having the copper-tin-zinc alloy plating layer was immersed in a plating solution having the composition below. A palladium strike  
25 plating layer (flash plating) was formed in a thickness of

0.2  $\mu\text{m}$  on the copper-tin-zinc alloy plating layer surface by electroplating under the plating conditions below. The plated base article was washed with water.

《Palladium Strike Plating》

5 〈Plating Solution Composition〉

Pure palladium 1-3 g/lit.

〈Plating Conditions〉

pH 8

Solution temperature 32°C

10 Current density (Dk) 3-5 A/dm<sup>2</sup>

Time 30 seconds

This plated base article was set in a sputtering apparatus, and the surface of the base article was cleaned by bombard cleaning in an argon atmosphere.

15 On the surface of the palladium strike plating layer formed on this base article surface, a titanium plating layer was formed in a thickness of 0.2-0.5  $\mu\text{m}$  by a sputtering method under the layer formation conditions below.

20 〈Layer Formation Conditions〉

Target: Titanium

Sputtering gas: Argon gas

Layer formation pressure: 0.2-0.9 Pa

Target power: 1.0-2.0 kW

25 Bias voltage: Ground to -300 V

On the surface of the titanium plating layer formed on this base article surface, a titanium carbide plating layer was formed in a thickness of  $0.4\mu\text{m}$  by a sputtering method under the layer formation conditions below.

5   〈Layer Formation Conditions〉

Target:	Titanium
Sputtering gas:	Gas mixture of argon and $\text{C}_2\text{H}_4$
Layer formation pressure:	0.2-0.9 Pa
Target power:	1.0-2.0 kW
10   Bias voltage:	Ground to -300 V

On the surface of the titanium carbide plating layer formed on this base article, a white-colored stainless steel coating layer was formed in a thickness of  $0.5\mu\text{m}$  by a sputtering method under the layer formation conditions below to obtain a watchband.

15   〈Layer Formation Conditions〉

Target:	Austenitic stainless steel SUS310S
Sputtering gas:	Argon gas
Layer formation pressure:	0.2-0.9 Pa
20   Target power:	1.0-2.0 kW
Bias voltage:	Ground to -300 V

The resulting watchband was tested for the corrosion resistance of the plating layer according to the aforementioned method. The rating number was not lower than 9.8, showing that the corrosion resistance was "good".

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(Example 25)

A watchband was produced in the same manner as in Example 24 except that a gas mixture of argon and  $\text{CH}_4$  was used as the sputtering gas in formation of the titanium carbide plating layer by sputtering.

The resulting watchband was tested for the corrosion resistance of the plating layer according to the aforementioned method. The rating number was not lower than 9.8, showing that the corrosion resistance was "good".

(Example 26)

A watchband was produced in the same manner as in Example 24 except that a gas mixture of argon and  $\text{C}_6\text{H}_6$  was used as the sputtering gas in formation of the titanium carbide plating layer by sputtering.

The resulting watchband was tested for the corrosion resistance of the plating layer according to the aforementioned method. The rating number was not lower than 9.8, showing that the corrosion resistance was "good".

(Example 27)

A base article of a watchcase was shaped from zinc by machining. This base article was washed and degreased with an organic solvent.

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The watchcase base article was immersed in a plating solution having the composition below. A copper-tin alloy plating layer (alloy metal ratio: Cu, 75 wt%; Sn, 20 wt%; and Zn, 5 wt%) was formed in a thickness of  $3\mu\text{m}$  on the base article surface by electroplating under the plating conditions below. The plated article was washed with water.

«Copper-Tin Alloy Plating»

〈Plating Solution Composition〉

10	Copper cyanide	15 g/lit. (in terms of Cu)
	Sodium stannate	15 g/lit. (in terms of Sn)
	Zinc cyanide	1 g/lit. (in terms of Zn)
	KOH	20 g/lit.
	KCN (free)	30 g/lit.
15	Brightener B (trade name)	10 ml/lit.

(produced by Nippon Shin-Kinzoku K.K.)

〈Plating Conditions〉

	pH	12.5 (at $50^{\circ}\text{C}$ )
	Solution temperature	$50^{\circ}\text{C}$
20	Current density (Dk)	$2.0\text{ A/dm}^2$
	Electrolysis time	12 minutes
	Stirring of plating solution	Rotation of rack of cathode rocker type

This watchcase base article having the copper-tin alloy plating layer was immersed in a plating solution

having the composition below. A copper-tin-zinc alloy  
 plating layer (alloy metal ratio: Cu, 50 wt%; Sn, 35 wt%,  
 and Zn, 15 wt%) was formed in a thickness of  $2.5\mu\text{m}$  on the  
 copper-tin alloy plating layer surface by electroplating  
 5 under the plating conditions below. The plated base  
 article was washed with water.

《Copper-Tin-Zinc Alloy Plating》

〈Plating Solution Composition〉

	Copper cyanide	8.5 g/lit. (in terms of Cu)
10	Sodium stannate	34.0 g/lit. (in terms of Sn)
	Zinc cyanide	1.0 g/lit. (in terms of Zn)
	KOH	20 g/lit.
	KCN (free)	50 g/lit.
	Brightener 1-1 (trade name)	0.5 ml/lit.
15		(produced by Degussa Japan Co., Ltd.)
	Brightener 2 (trade name)	0.5 ml/lit.
		(produced by Degussa Japan Co., Ltd.)

〈Plating Conditions〉

	pH	13.0 (at $60^{\circ}\text{C}$ )
20	Solution temperature	$60.0^{\circ}\text{C}$
	Current density (Dk)	$2.0\text{ A/dm}^2$
	Electrolysis time	15 minutes

This watchcase article having the copper-tin-zinc  
 alloy plating layer was immersed in a plating solution  
 25 having the composition below. A gold strike plating layer





Target power: 1.0-2.0 kW  
Bias voltage: Ground to -300 V

On the surface of the titanium plating layer formed on this base article surface, a white-colored stainless steel coating layer was formed in a thickness of  $0.3\mu\text{m}$  by a sputtering method under the layer formation conditions below to obtain a watchcase.

(Layer Formation Conditions)

Target: Austenitic stainless steel SUS310S  
Sputtering gas: Argon gas  
Layer formation pressure: 0.2-0.9 Pa  
Target power: 1.0-2.0 kW  
Bias voltage: Ground to -300 V

The resulting watchcase was tested for the corrosion resistance of the plating layer according to the aforementioned method. The rating number was not lower than 9.8, showing that the corrosion resistance was "good".

(Example 28)

A base article of a watchband was shaped from brass by machining. The base article was washed and degreased with an organic solvent.

This base article was immersed in a plating solution having the composition below. A nickel strike plating layer (flash plating) was formed in a thickness of

0.1-0.2  $\mu\text{m}$  on the base article surface by electroplating under the plating conditions below. The plated article was washed with water.

《Nickel Strike Plating》

5 <Plating Solution Composition>

Nickel chloride 180 g/lit.

Hydrochloric acid 100 g/lit.

<Plating Conditions>

pH 0.3 to 1

10 Solution temperature Room temperature

Current density (Dk) 3-5 A/dm<sup>2</sup>

Time 30-60 seconds

This watchband base article having a nickel strike plating layer was immersed in a plating solution having the composition below. A nickel plating layer was formed in a thickness of 2  $\mu\text{m}$  on the nickel strike plating layer surface by electroplating under the plating conditions below. The plated base article was washed with water.

《Nickel Plating》

20 <Plating Solution Composition>

Nickel sulfate 250 g/lit.

Nickel chloride 75 g/lit.

Boric acid 50 g/lit.

Brightener (Brightener #61, produced by Ebara-Udylite Co., Ltd.)

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pH 3.6-4.0

Solution temperature 40-50°C.

5      Current density (Dk)      3 A/dm<sup>2</sup>

This watchband base article having a nickel plating layer was immersed in a plating solution having the composition below. A nickel-phosphorus alloy plating layer was formed in a thickness of  $2\mu\text{m}$  on the nickel plating layer surface by electroplating under the plating conditions below. The plated base article was washed with water.

## 《Nickel-Phosphorus Alloy Plating》

(Plating Solution Composition)

15	Nickel sulfate	40-50 g/lit.
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Nickel hydroxide                      10-20 g/lit.

Sodium hypophosphite                      3-10 g/lit.

Phosphoric acid 10-20 ml/lit.

Sodium citrate                      30-50 g/lit.

## 20 (Plating Conditions)

pH 2.6-3.2

Solution temperature . 55°C

Current density (Dk) :  $2 \text{ A/dm}^2$

This watchband base article having the nickel-  
25 phosphorus alloy plating layer was immersed in a plating

solution having the composition below. A palladium strike plating layer (flash plating) was formed in a thickness of  $0.2\mu\text{m}$  on the nickel-phosphorus alloy plating layer surface by electroplating under the plating conditions below. The plated base article was washed with water, and dried.

《Palladium Strike Plating》

〈Plating Solution Composition〉

Pure palladium 1-3 g/lit.

10 〈Plating Conditions〉

pH 8

Solution temperature  $32^{\circ}\text{C}$

Current density (Dk)  $3-5\text{ A/dm}^2$

Time 30 seconds

15 This plated base article was set in a sputtering apparatus, and the surface of the base article was cleaned by bombard cleaning in an argon atmosphere.

On the surface of the palladium strike plating layer formed on this base article surface, a white-colored stainless steel coating layer was formed in a thickness of  $0.5\mu\text{m}$  by a sputtering method under the layer formation conditions below.

〈Layer Formation Conditions〉

Target: Austenitic stainless steel SUS310S

25 Sputtering gas: Argon gas

Layer formation pressure: 0.2-0.9 Pa  
Target power: 1.0-2.0 kW  
Bias voltage: Ground to -300 V

Then in this apparatus, the above nickel-phosphorus alloy plating layer was subjected to heat treatment (age hardening treatment) at 250°C for 30 minutes to obtain a watchband.

The obtained watchband had a surface hardness of 650 (HV; Vickers hardness tester, 25 g, impression time of 10 seconds).

Another watchband was produced in the same manner as above by forming a white-colored stainless steel coating layer of 2 μm thick and heat-treating the nickel-phosphorus alloy plating layer in the same manner as above.

This watchband had a surface hardness of 650 (HV; Vickers hardness tester, 25 g, impression time of 10 seconds).

These watchbands were immersed in a plating solution having the composition below. A palladium flash plating layer was formed in a thickness of 0.2 μm on the stainless steel coating layer surface by electroplating under the plating conditions below. The plated base article was washed with water, and dried.

《Palladium Flash Plating》

25 <Plating Solution Composition>

Pure palladium 1-3 g/lit.

〈Plating Conditions〉

pH 8

Solution temperature 32°C

5 Current density (Dk) 3-5 A/dm<sup>2</sup>

Time 30 seconds

The resulting watchbands were tested for the corrosion resistance of the plating layer according to the aforementioned method. The rating numbers were not lower than 9.8, showing that the corrosion resistance was "good".

(Example 29)

A base article of a watchband was shaped from brass by machining. This base article was washed and degreased with an organic solvent.

The watchband base article was immersed in a plating solution having the composition below. A copper-tin alloy plating layer (alloy metal ratio: Cu, 75 wt%; Sn, 20 wt%; and Zn, 5 wt%) was formed in a thickness of 3 μm on the base article surface by electroplating under the plating conditions below. The plated article was washed with water.

《Copper-Tin Alloy Plating》

〈Plating Solution Composition〉

25 Copper cyanide 15 g/lit. (in terms of Cu)

	Sodium stannate	15 g/lit. (in terms of Sn)
	Zinc cyanide	1 g/lit. (in terms of Zn)
	KOH	20 g/lit.
	KCN (free)	30 g/lit.
5	Brightener B (trade name)	10 ml/lit.

(produced by Nippon Shin-Kinzoku K.K.)

〈Plating Conditions〉

	pH	12.5 (at 50°C)
	Solution temperature	50°C
10	Current density (Dk)	2.0 A/dm <sup>2</sup>
	Electrolysis time	12 minutes
	Stirring of plating solution	Rotation of rack of cathode rocker type

This watchband base article having the copper-tin alloy plating layer was immersed in a plating solution having the composition below. A copper-tin-zinc alloy plating layer (alloy metal ratio: Cu, 50 wt%; Sn, 35 wt%, and Zn, 15 wt%) was formed in a thickness of 2.5 μm on the copper-tin alloy plating layer surface by electroplating under the plating conditions below. The plated base article was washed with water.

《Copper-Tin-Zinc Alloy Plating》

〈Plating Solution Composition〉

	Copper cyanide	8.5 g/lit. (in terms of Cu)
25	Sodium stannate	34.0 g/lit. (in terms of Sn)

Zinc cyanide 1.0 g/lit. (in terms of Zn)

KOH 20 g/lit.

KCN (free) 50 g/lit.

Brightener 1-1 (trade name) 0.5 ml/lit.

5 (produced by Degussa Japan Co., Ltd.)

Brightener 2 (trade name) 0.5 ml/lit.

(produced by Degussa Japan Co., Ltd.)

〈Plating Conditions〉

pH 13.0 (at 60°C)

10 Solution temperature 60.0°C

Current density (Dk) 2.0 A/dm<sup>2</sup>

Electrolysis time 15 minutes

This watchband base article having the copper-tin-zinc alloy plating layer was immersed in a plating solution having the composition below. A palladium strike plating layer (flash plating) was formed in a thickness of 0.2 μm on the copper-tin-zinc alloy plating layer surface by electroplating under the plating conditions below. The plated base article was washed with water.

20 «Palladium Strike Plating»

〈Plating Solution Composition〉

Pure palladium 1-3 g/lit.

〈Plating Conditions〉

pH 8

25 Solution temperature 32°C

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Current density (Dk)	3-5 A/dm <sup>2</sup>
Time	30 seconds

This plated base article was set in a sputtering apparatus, and the surface of the base article was cleaned  
5 by bombard cleaning in an argon atmosphere.

On the surface of the palladium strike plating layer formed on this base article surface, a white-colored stainless steel coating layer was formed in a thickness of 1.0  $\mu$ m by a sputtering method under the layer formation  
10 conditions below to obtain a watchband.

〈Layer Formation Conditions〉

Target:	Austenitic stainless steel SUS310S
Sputtering gas:	Argon gas
Layer formation pressure:	0.2-0.9 Pa
15 Target power:	1.0-2.0 kW
Bias voltage:	Ground to -300 V

This watchband was immersed in a plating solution having the composition below. A palladium flash plating layer was formed in a thickness of 0.2  $\mu$ m on the stainless  
20 steel plating layer surface by electroplating under the plating conditions below. The plated base article was washed with water and dried.

《Palladium Flash Plating》

〈Plating Solution Composition〉

25 Pure palladium	1-3 g/lit.
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## (Plating Conditions)

pH	8
Solution temperature	32°C
Current density (Dk)	3-5 A/dm <sup>2</sup>
5 Time	30 seconds

The resulting watchband was tested for the corrosion resistance of the plating layer according to the aforementioned method. The rating number was not lower than 9.8, showing that the corrosion resistance was "good".

10 The personal ornaments (of the present invention) obtained in the above Examples 1-29 were evaluated for abrasion resistance with an abrasion resistance tester NUS-ISO-2 (trade name, manufactured by Suga Shikenki K.K.)

15 according to the procedure described below.

As the evaluation standard for the abrasion resistance of the personal ornaments derived in Examples 1-29, a conventional personal ornament sample was prepared which has been on the market and has not caused any

20 complaints. Specifically, a brass base article having a polished surface of surface roughness (Ra) of 0.05-0.5  $\mu$ m and having a thickness of 1 mm was coated with a nickel plating layer of 3  $\mu$ m thick and a palladium-nickel alloy plating layer of 1  $\mu$ m thick successively as the underlying

25 plating layers and was further coated with a gold-nickel

alloy plating layer of  $0.8\mu\text{m}$  thick and gold-iron alloy plating layer of  $0.2\mu\text{m}$  thick successively as the finish-plating layers (hereinafter referred to as HGP).

Table 1 shows the test results. In the abrasion resistance tests, none of the personal ornaments of Examples 1-29 caused the exposure of the underlying plating layer even after test abrasion of 200 times.

〈Abrasion Resistance Test〉

As shown in Fig. 1, a test piece 1 having a coating layer is fixed with a test piece-pressing plate 2 and test piece-pressing screws 3 at the aperture portion of the test piece mount 4 with the coated face side directed downward. An abrasive paper sheet (not shown in the drawing) is attached to the abrasion wheel 5. A load is applied upward to the abrasion wheel 5 by means of a balance mechanism not shown in the drawing to press the abrasive paper sheet against the test piece 1.

In this state, the test piece mount 4 is moved reciprocatingly by a mechanism of converting the rotation of a motor not shown in the drawing to reciprocation movement. The abrasion wheel 5 is rotated intermittently in the arrow direction by 0.9 degree per each one reciprocation movement of the test piece mount 4. By this rotation of the abrasion wheel, the abrasion paper sheet on the abrasion wheel 5 is pressed at the unabraded fresh

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portion against the test piece 1. The times of the reciprocation of the test piece mount 4 can be automatically preset to stop the abrasion test at a prescribed times of the reciprocation.

5 In practice of the abrasion test, a wrapping film (having  $\text{Cr}_2\text{O}_3$  particles of particle diameter of  $0.5\mu\text{m}$  on the film surface) was used as the abrasion paper sheet; the contact load of the abrasion paper sheet against the test piece 1 was set at 500 g; and the reciprocation of  
10 the test piece mount 4 was conducted 200 times. At the time when the underlying plating layer of the test piece 1 came to be exposed, the abrasion test was stopped.

The abrasion resistance in the present invention was evaluated in comparison with the abrasion resistance  
15 level of the aforementioned HGP which has been on the market and has not caused any complaints. The level of the abrasion resistance equal to or higher than that of the HGP is evaluated to be "good", and the one lower than that is evaluated to be "poor".

20

Table 1

5		Number of test pieces having <u>underlying plating layer exposed</u>		Evaluation of abrasion resistance
		Number of repetition of abrasion 200 to 250 times	251 to 300 times	
	Example 1	1	4	good
10	Example 2	0	5	good
	Example 3	0	5	good
	Example 4	0	5	good
	Example 5	0	5	good
	Example 6	1	4	good
15	Example 7	0	5	good
	Example 8	0	5	good
	Example 9	0	5	good
	Example 10	0	5	good
	Example 11	0	5	good
20	Example 12	0	5	good
	Example 13	0	5	good
	Example 14	0	5	good
	Example 15	0	5	good
	Example 16	0	5	good
25	Example 17	0	5	good
	Example 18	1	4	good
	Example 19	0	5	good
	Example 20	1	4	good
	Example 21	0	5	good
30	Example 22	0	5	good
	Example 23	1	4	good
	Example 24	0	5	good
	Example 25	0	5	good
	Example 26	0	5	good
35	Example 27	0	5	good
	Example 28	0	5	good
	Example 29	0	5	good
	Reference (HGP)	2	3	--

40 (Note) Number of test sample pieces = 5